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The Ideal Gas Law

Foundation

We assume as our starting point the atomic molecular theory. That is, we assume that all matter is composed of discrete particles. The elements consist of identical atoms, and compounds consist of identical molecules, which are particles containing small whole number ratios of atoms. We also assume that we have determined a complete set of relative atomic weights, allowing us to determine the molecular formula for any compound.

Goals

The individual molecules of different compounds have characteristic properties, such as mass, structure, geometry, bond lengths, bond angles, polarity, diamagnetism or paramagnetism. We have not yet considered the properties of mass quantities of matter, such as density, phase (solid, liquid or gas) at room temperature, boiling and melting points, reactivity, and so forth. These are properties which are not exhibited by individual molecules. It makes no sense to ask what the boiling point of one molecule is, nor does an individual molecule exist as a gas, solid, or liquid. However, we do expect that these material or bulk properties are related to the properties of the individual molecules. Our ultimate goal is to relate the properties of the atoms and molecules to the properties of the materials which they comprise.

Achieving this goal will require considerable analysis. In this Concept Development Study, we begin at a somewhat more fundamental level, with our goal to know more about the nature of gases, liquids and solids. We need to study the relationships between the physical properties of materials, such as density and temperature. We begin our study by examining these properties in gases.

Observation 1: Pressure-Volume Measurements on Gases

It is an elementary observation that air has a "spring" to it: if you squeeze a balloon, the balloon rebounds to its original shape. As you pump air into a

bicycle tire, the air pushes back against the piston of the pump. Furthermore, this resistance of the air against the piston clearly increases as the piston is pushed farther in. The "spring" of the air is measured as a pressure, where the pressure P is defined

Equation:

$$P = \frac{F}{A}$$

F is the force exerted by the air on the surface of the piston head and A is the surface area of the piston head.

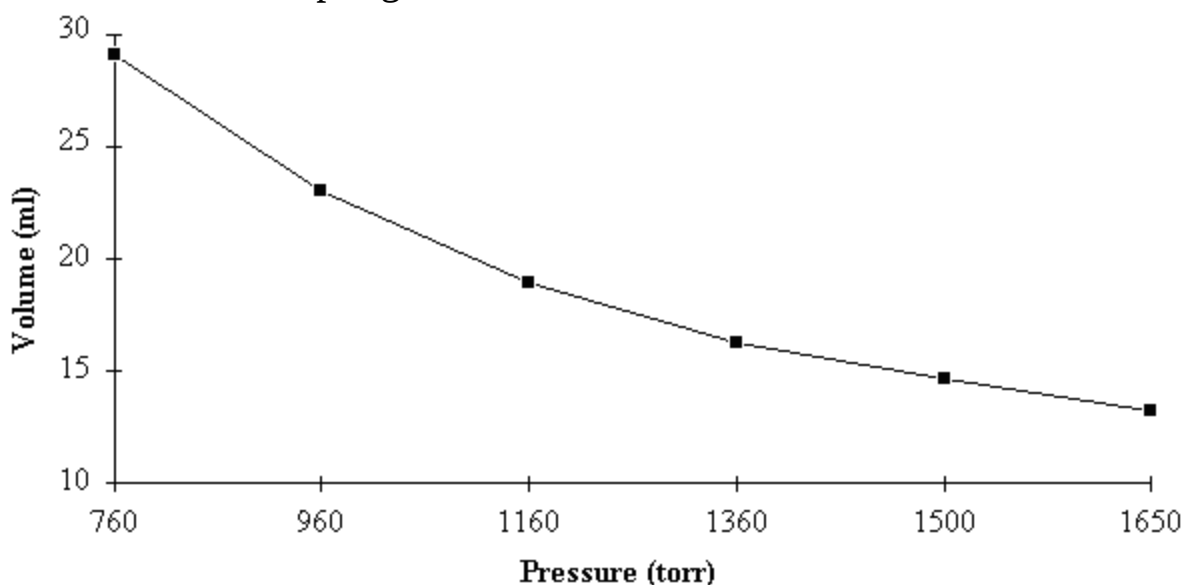
For our purposes, a simple pressure gauge is sufficient. We trap a small quantity of air in a syringe (a piston inside a cylinder) connected to the pressure gauge, and measure both the volume of air trapped inside the syringe and the pressure reading on the gauge. In one such sample measurement, we might find that, at atmospheric pressure (760 torr), the volume of gas trapped inside the syringe is 29.0 ml. We then compress the syringe slightly, so that the volume is now 23.0 ml. We feel the increased spring of the air, and this is registered on the gauge as an increase in pressure to 960 torr. It is simple to make many measurements in this manner. A sample set of data appears in [\[link\]](#). We note that, in agreement with our experience with gases, the pressure increases as the volume decreases. These data are plotted [here](#).

Pressure (torr)	Volume (ml)
760	29.0
960	23.0

Pressure (torr)	Volume (ml)
1160	19.0
1360	16.2
1500	14.7
1650	13.3

Sample Data from Pressure-Volume Measurement

Measurements on Spring of the Air

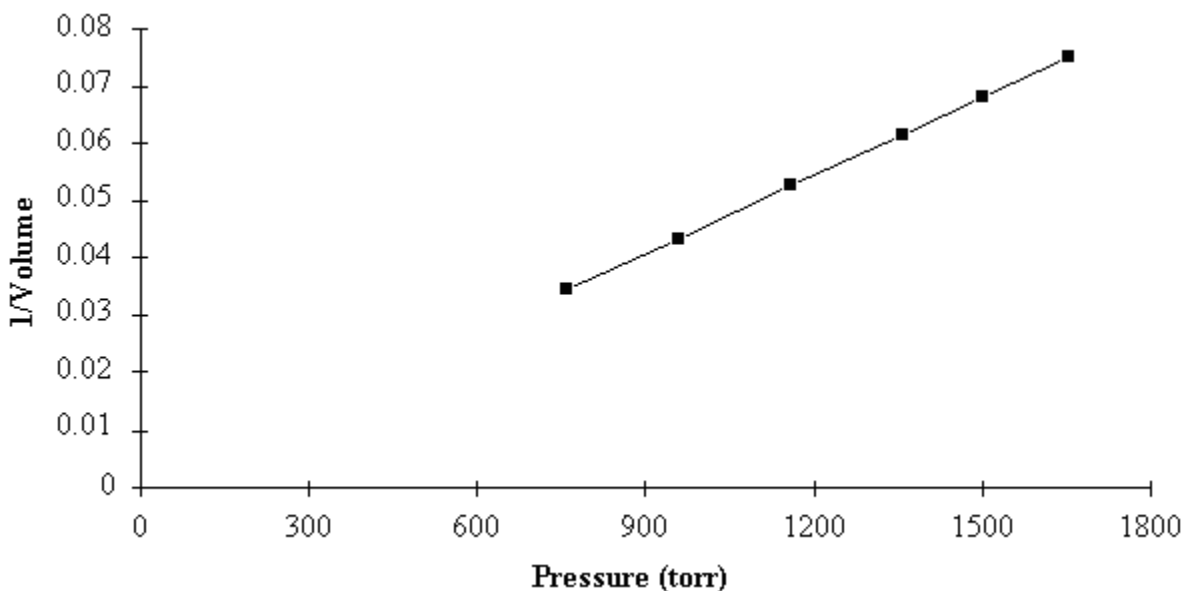


An initial question is whether there is a quantitative relationship between the pressure measurements and the volume measurements. To explore this possibility, we try to plot the data in such a way that both quantities increase together. This can be accomplished by plotting the pressure versus the inverse of the volume, rather than versus the volume. The data are given in [\[link\]](#) and plotted [here](#).

Pressure (torr)	Volume (ml)	1/Volume (1/ml)	Pressure × Volume
760	29.0	0.0345	22040
960	23.0	0.0435	22080
1160	19.0	0.0526	22040
1360	16.2	0.0617	22032
1500	14.7	0.0680	22050
1650	13.3	0.0752	21945

Analysis of Sample Data

Analysis of Measurements on Spring of the Air



Notice also that, with elegant simplicity, the data points form a straight line. Furthermore, the straight line seems to connect to the origin $\{0, 0\}$. This means that the pressure must simply be a constant multiplied by $\frac{1}{V}$:

Equation:

$$P = k \times \frac{1}{V}$$

If we multiply both sides of this equation by V , then we notice that
Equation:

$$PV = k$$

In other words, if we go back and multiply the pressure and the volume together for each experiment, we should get the same number each time. These results are shown in the last column of [\[link\]](#), and we see that, within the error of our data, all of the data points give the same value of the product of pressure and volume. (The volume measurements are given to three decimal places and hence are accurate to a little better than 1%. The values of Pressure \times Volume are all within 1% of each other, so the fluctuations are not meaningful.)

We should wonder what significance, if any, can be assigned to the number 22040 (torr ml) we have observed. It is easy to demonstrate that this "constant" is not so constant. We can easily trap any amount of air in the syringe at atmospheric pressure. This will give us any volume of air we wish at 760 torr pressure. Hence, the value 22040 (torr ml) is only observed for the particular amount of air we happened to choose in our sample measurement. Furthermore, if we heat the syringe with a fixed amount of air, we observe that the volume increases, thus changing the value of the 22040 (torr ml). Thus, we should be careful to note that the **product of pressure and volume is a constant for a given amount of air at a fixed temperature**. This observation is referred to as **Boyle's Law**, dating to 1662.

The data given in [\[link\]](#) assumed that we used air for the gas sample. (That, of course, was the only gas with which Boyle was familiar.) We now experiment with varying the composition of the gas sample. For example, we can put oxygen, hydrogen, nitrogen, helium, argon, carbon dioxide, water vapor, nitrogen dioxide, or methane into the cylinder. In each case we start with 29.0 ml of gas at 760 torr and 25°C. We then vary the volumes as

in [\[link\]](#) and measure the pressures. Remarkably, we find that the pressure of each gas is exactly the same as every other gas at each volume given. For example, if we press the syringe to a volume of 16.2 ml, we observe a pressure of 1360 torr, no matter which gas is in the cylinder. This result also applies equally well to mixtures of different gases, the most familiar example being air, of course.

We conclude that the pressure of a gas sample depends on the volume of the gas and the temperature, but not on the composition of the gas sample. We now add to this result a conclusion from a [previous study](#). Specifically, we recall the [Law of Combining Volumes](#), which states that, when gases combine during a chemical reaction at a fixed pressure and temperature, the ratios of their volumes are simple whole number ratios. We further recall that this result can be explained in the context of the atomic molecular theory by hypothesizing that equal volumes of gas contain equal numbers of gas particles, independent of the type of gas, a conclusion we call **Avogadro's Hypothesis**. Combining this result with Boyle's law reveals that the **pressure** of a gas depends on the **number** of gas particles, the **volume** in which they are contained, and the **temperature** of the sample. The pressure does **not** depend on the type of gas particles in the sample or whether they are even all the same.

We can express this result in terms of Boyle's law by noting that, in the equation $PV = k$, the "constant" k is actually a function which varies with both number of gas particles in the sample and the temperature of the sample. Thus, we can more accurately write

Equation:

$$PV = k(N, t)$$

explicitly showing that the product of pressure and volume depends on N , the number of particles in the gas sample, and t , the temperature.

It is interesting to note that, in 1738, Bernoulli showed that the inverse relationship between pressure and volume could be proven by assuming that a gas consists of individual particles colliding with the walls of the container. However, this early evidence for the existence of atoms was

ignored for roughly 120 years, and the atomic molecular theory was not to be developed for another 70 years, based on mass measurements rather than pressure measurements.

Observation 2: Volume-Temperature Measurements on Gases

We have already noted the dependence of Boyle's Law on temperature. To observe a constant product of pressure and volume, the temperature must be held fixed. We next analyze what happens to the gas when the temperature is allowed to vary. An interesting first problem that might not have been expected is the question of how to measure temperature. In fact, for most purposes, we think of temperature only in the rather non-quantitative manner of "how hot or cold" something is, but then we measure temperature by examining the length of mercury in a tube, or by the electrical potential across a thermocouple in an electronic thermometer. We then briefly consider the complicated question of just what we are measuring when we measure the temperature.

Imagine that you are given a cup of water and asked to describe it as "hot" or "cold." Even without a calibrated thermometer, the experiment is simple: you put your finger in it. Only a qualitative question was asked, so there is no need for a quantitative measurement of "how hot" or "how cold." The experiment is only slightly more involved if you are given two cups of water and asked which one is hotter or colder. A simple solution is to put one finger in each cup and to directly compare the sensation. You still don't need a calibrated thermometer or even a temperature scale at all.

Finally, imagine that you are given a cup of water each day for a week at the same time and are asked to determine which day's cup contained the hottest or coldest water. Since you can no longer trust your sensory memory from day to day, you have no choice but to define a temperature scale. To do this, we make a physical measurement on the water by bringing it into contact with something else whose properties depend on the "hotness" of the water in some unspecified way. (For example, the volume of mercury in a glass tube expands when placed in hot water; certain strips of metal expand or contract when heated; some liquid crystals change color when heated; etc.) We assume that this property will have the same value when it

is placed in contact with two objects which have the same "hotness" or temperature. Somewhat obliquely, this defines the temperature measurement.

For simplicity, we illustrate with a mercury-filled glass tube thermometer. We observe quite easily that when the tube is inserted in water we consider "hot," the volume of mercury is larger than when we insert the tube in water that we consider "cold." Therefore, the volume of mercury is a measure of how hot something is. Furthermore, we observe that, when two very different objects appear to have the same "hotness," they also give the same volume of mercury in the glass tube. This allows us to make quantitative comparisons of "hotness" or temperature based on the volume of mercury in a tube.

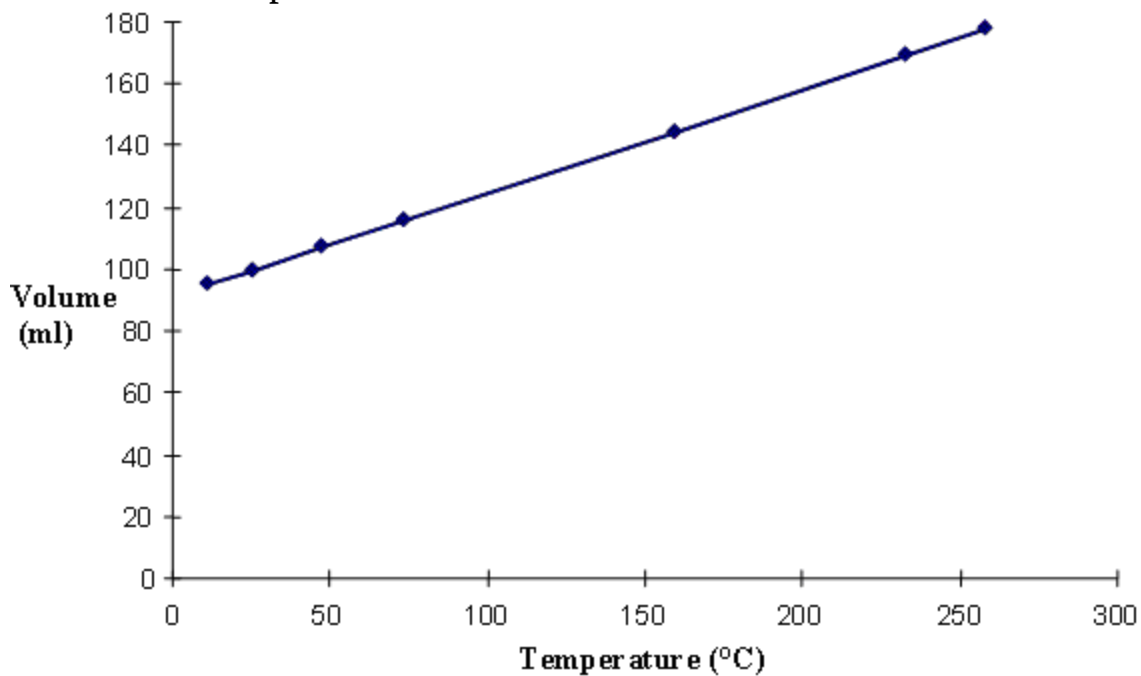
All that remains is to make up some numbers that define the scale for the temperature, and we can literally do this in any way that we please. This arbitrariness is what allows us to have two different, but perfectly acceptable, temperature scales, such as Fahrenheit and Centigrade. The latter scale simply assigns zero to be the temperature at which water freezes at atmospheric pressure. We then insert our mercury thermometer into freezing water, and mark the level of the mercury as "0". Another point on our scale assigns 100 to be the boiling point of water at atmospheric pressure. We insert our mercury thermometer into boiling water and mark the level of mercury as "100." Finally, we just mark off in increments of $\frac{1}{100}$ of the distance between the "0" and the "100" marks, and we have a working thermometer. Given the arbitrariness of this way of measuring temperature, it would be remarkable to find a quantitative relationship between temperature and any other physical property.

Yet that is what we now observe. We take the same syringe used in the previous section and trap in it a small sample of air at room temperature and atmospheric pressure. (From our observations above, it should be clear that the type of gas we use is irrelevant.) The experiment consists of measuring the volume of the gas sample in the syringe as we vary the temperature of the gas sample. In each measurement, the pressure of the gas is held fixed by allowing the piston in the syringe to move freely against atmospheric pressure. A sample set of data is shown in [\[link\]](#) and plotted [here](#).

Temperature (°C)	Volume (ml)
11	95.3
25	100.0
47	107.4
73	116.1
159	145.0
233	169.8
258	178.1

Sample Data from Volume-Temperature Measurement

Volume vs. Temperature of a Gas



We find that there is a simple linear (straight line) relationship between the volume of a gas and its temperature as measured by a mercury thermometer.

We can express this in the form of an equation for a line:

Equation:

$$V = \alpha t + \beta$$

where V is the volume and t is the temperature in $^{\circ}\text{C}$. α and β are the slope and intercept of the line, and in this case, $\alpha = 0.335$ and, $\beta = 91.7$. We can rewrite this equation in a slightly different form:

Equation:

$$V = \alpha \left(t + \frac{\beta}{\alpha} \right)$$

This is the same equation, except that it reveals that the quantity $\frac{\beta}{\alpha}$ must be a temperature, since we can add it to a temperature. This is a particularly important quantity: if we were to set the temperature of the gas equal to $-\frac{\beta}{\alpha} = -273^{\circ}\text{C}$, we would find that the volume of the gas would be exactly 0! (This assumes that this equation can be extrapolated to that temperature. This is quite an optimistic extrapolation, since we haven't made any measurements near to -273°C . In fact, our gas sample would condense to a liquid or solid before we ever reached that low temperature.)

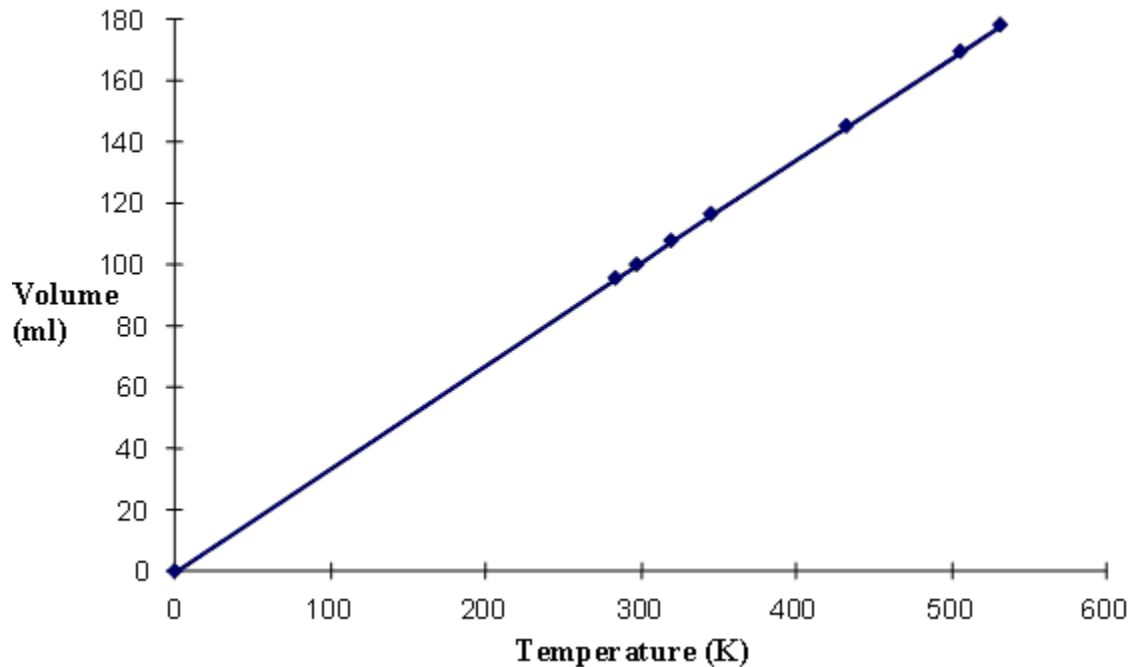
Since the volume depends on the pressure and the amount of gas (Boyle's Law), then the values of α and β also depend on the pressure and amount of gas and carry no particular significance. However, when we repeat our observations for many values of the amount of gas and the fixed pressure, we find that the **ratio** $-\frac{\beta}{\alpha} = -273^{\circ}\text{C}$ does not vary from one sample to the next. Although we do not know the physical significance of this temperature at this point, we can assert that it is a true constant, independent of any choice of the conditions of the experiment. We refer to this temperature as **absolute zero**, since a temperature below this value would be predicted to produce a negative gas volume. Evidently, then, we cannot expect to lower the temperature of any gas below this temperature.

This provides us an "absolute temperature scale" with a zero which is not arbitrarily defined. This we define by adding 273 (the value of $\frac{\beta}{\alpha}$) to temperatures measured in °C, and we define this scale to be in units of degrees Kelvin (K). The data in [\[link\]](#) are now recalibrated to the absolute temperature scale in [\[link\]](#) and plotted [here](#).

Temperature (°C)	Temperature (K)	Volume (ml)
11	284	95.3
25	298	100.0
47	320	107.4
73	350	116.1
159	432	145.0
233	506	169.8
258	531	178.1

Analysis of Volume-Temperature Data

Volume vs. Absolute Temperature of a Gas



Note that **the volume is proportional to the absolute temperature** in degrees Kelvin,

Equation:

$$V = kT$$

provided that the pressure and amount of gas are held constant. This result is known as **Charles' Law**, dating to 1787.

As with Boyle's Law, we must now note that the "constant" k is not really constant, since the volume also depends on the pressure and quantity of gas. Also as with Boyle's Law, we note that Charles' Law does not depend on the **type** of gas on which we make the measurements, but rather depends only the number of particles of gas. Therefore, we slightly rewrite Charles' Law to explicit indicate the dependence of k on the pressure and number of particles of gas

Equation:

$$V = k(N, P)T$$

The Ideal Gas Law

We have been measuring four properties of gases: pressure, volume, temperature, and "amount", which we have assumed above to be the number of particles. The results of three observations relate these four properties pairwise. Boyle's Law relates the pressure and volume at constant temperature and amount of gas:

Equation:

$$P \times V = k_1(N, T)$$

Charles' Law relates the volume and temperature at constant pressure and amount of gas:

Equation:

$$V = k_2(N, P)T$$

The Law of Combining Volumes leads to Avogadro's Hypothesis that the volume of a gas is proportional to the number of particles (N) provided that the temperature and pressure are held constant. We can express this as

Equation:

$$V = k_3(P, T)N$$

We will demonstrate below that these three relationships can be combined into a single equation relating P , V , T , and N . Jumping to the conclusion, however, we can more easily show that these three relationships can be considered as special cases of the more general equation known as the **Ideal Gas Law**:

Equation:

$$PV = nRT$$

where R is a constant, n is the number of moles of gas, related to the number of particles N by Avogadro's number, N_A

Equation:

$$n = \frac{N}{N_A}$$

In Boyle's Law, we examine the relationship of P and V when n (or N) and T are fixed. In the Ideal Gas Law, when n and T are constant, nRT is constant, so the product PV is also constant. Therefore, Boyle's Law is a special case of the Ideal Gas Law. If n and P are fixed in the Ideal Gas Law, then $V = \frac{nR}{P} T$ and $\frac{nR}{P}$ is a constant. Therefore, Charles' Law is also a special case of the Ideal Gas Law. Finally, if P and T are constant, then in the Ideal Gas Law, $V = \frac{RT}{P} n$ and the volume is proportional the number of moles or particles. Hence, Avogadro's hypothesis is a special case of the Ideal Gas Law.

We have now shown that the each of our experimental observations is consistent with the Ideal Gas Law. We might ask, though, how did we get the Ideal Gas Law? We would like to derive the Ideal Gas Law from the three experiemental observations. To do so, we need to learn about the functions $k_1(N, T)$, $k_2(N, P)$, $k_3(P, T)$.

We begin by examining Boyle's Law in more detail: if we hold N and P fixed in Boyle's Law and allow T to vary, the volume must increase with the temperature in agreement with Charles' Law. In other words, with N and P fixed, the volume must be proportional to T . Therefore, k_1 in Boyle's Law must be proportional to T :

Equation:

$$k_1(N, T) = k_4(N) \times T$$

where k_4 is a new function which depends only on N . [\[link\]](#) then becomes

Equation:

$$P \times V = k_4(N)T$$

Avogadro's Hypothesis tells us that, at constant pressure and temperature, the volume is proportional to the number of particles. Therefore k_4 must also increase proportionally with the number of particles:

Equation:

$$k_4(N) = k \times N$$

where k is yet another new constant. In this case, however, there are no variables left, and k is truly a constant. Combining [\[link\]](#) and [\[link\]](#) gives

Equation:

$$P \times V = k \times N \times T$$

This is very close to the Ideal Gas Law, except that we have the number of particles, N , instead of the number of moles, n . We put this result in the more familiar form by expressing the number of particles in terms of the number of moles, n , by dividing the number of particles by Avogadro's number, N_A , from [\[link\]](#). Then, from [\[link\]](#),

Equation:

$$P \times V = k \times N_A \times n \times T$$

The two constants, k and N_A , can be combined into a single constant, which is commonly called R , the gas constant. This produces the familiar conclusion of [\[link\]](#).

Observation 3: Partial Pressures

We referred briefly above to the pressure of mixtures of gases, noting in our measurements leading to Boyle's Law that the total pressure of the mixture depends only on the number of moles of gas, regardless of the types and amounts of gases in the mixture. The Ideal Gas Law reveals that the pressure exerted by a mole of molecules does not depend on what those molecules are, and our earlier observation about gas mixtures is consistent with that conclusion.

We now examine the actual process of mixing two gases together and measuring the total pressure. Consider a container of fixed volume 25.0L. We inject into that container 0.78 moles of N_2 gas at 298K. From the Ideal Gas Law, we can easily calculate the measured pressure of the nitrogen gas to be 0.763 atm. We now take an identical container of fixed volume 25.0L, and we inject into that container 0.22 moles of O_2 gas at 298K. The measured pressure of the oxygen gas is 0.215 atm. As a third measurement, we inject 0.22 moles of O_2 gas at 298K into the **first** container which already has 0.78 moles of N_2 . (Note that the mixture of gases we have prepared is very similar to that of air.) The measured pressure in this container is now found to be 0.975 atm.

We note now that the **total** pressure of the mixture of N_2 and O_2 in the container is equal to the sum of the pressures of the N_2 and O_2 samples taken separately. We now define the **partial pressure** of each gas in the mixture to be the pressure of each gas as if it were the only gas present. Our measurements tell us that the partial pressure of N_2 , P_{N_2} , is 0.763 atm, and the partial pressure of O_2 , P_{O_2} , is 0.215 atm.

With this definition, we can now summarize our observation by saying that the total pressure of the mixture of oxygen and nitrogen is equal to the sum of the partial pressures of the two gases. This is a general result: **Dalton's Law of Partial Pressures**.

Dalton's Law of Partial Pressures

The total pressure of a mixture of gases is the sum of the partial pressures of the component gases in the mixture

Review and Discussion Questions

Exercise:

Problem:

Sketch a graph with two curves showing Pressure vs. Volume for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.

Exercise:**Problem:**

Sketch a graph with two curves showing Pressure vs. $1/\text{Volume}$ for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.

Exercise:**Problem:**

Sketch a graph with two curves showing Volume vs. Temperature for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same pressure. Explain the comparison of the two curves.

Exercise:**Problem:**

Sketch a graph with two curves showing Volume vs Temperature for two different values of the pressure of the gas, with $P_2 > P_1$, both for the same number of moles. Explain the comparison of the two curves.

Exercise:**Problem:**

Explain the significance of the fact that, in the volume-temperature experiments, $\frac{\beta}{\alpha}$ is observed to have the same value, independent of the quantity of gas studied and the type of gas studied. What is the significance of the quantity $\frac{\beta}{\alpha}$? Why is it more significant than either β or α ?

Exercise:**Problem:**

Amonton's Law says that the pressure of a gas is proportional to the absolute temperature for a fixed quantity of gas in a fixed volume. Thus, $P = k(N, V)T$. Demonstrate that Amonton's Law can be derived by combining Boyle's Law and Charles' Law.

Exercise:**Problem:**

Using Boyle's Law in your reasoning, demonstrate that the "constant" in Charles' Law, i.e. $k_2(N, P)$, is inversely proportional to P .

Exercise:**Problem:**

Explain how Boyle's Law and Charles' Law may be combined to the general result that, for constant quantity of gas, $P \times V = kT$.

Exercise:**Problem:**

Using Dalton's Law and the Ideal Gas Law, show that the partial pressure of a component of a gas mixture can be calculated from

Equation:

$$P_i = PX_i$$

Where P is the total pressure of the gas mixture and X_i is the **mole fraction** of component i , defined by

Equation:

$$X_i = \frac{n_i}{n_{\text{total}}}$$

Exercise:**Problem:**

Dry air is 78.084% nitrogen, 20.946% oxygen, 0.934% argon, and 0.033% carbon dioxide. Determine the mole fractions and partial pressures of the components of dry air at standard pressure.

Exercise:

Problem: Assess the accuracy of the following statement:

"Boyle's Law states that $PV = k_1$, where k_1 is a constant. Charles' Law states that $V = k_2T$, where k_2 is a constant. Inserting V from Charles' Law into Boyle's Law results in $Pk_2T = k_1$. We can rearrange this to read $PT = \frac{k_1}{k_2} = \text{a constant}$. Therefore, the pressure of a gas is inversely proportional to the temperature of the gas."

In your assessment, you must determine what information is correct or incorrect, provide the correct information where needed, explain whether the reasoning is logical or not, and provide logical reasoning where needed.

The Kinetic Molecular Theory

Foundation

We assume an understanding of the atomic molecular theory postulates, including that all matter is composed of discrete particles. The elements consist of identical atoms, and compounds consist of identical molecules, which are particles containing small whole number ratios of atoms. We also assume that we have determined a complete set of relative atomic weights, allowing us to determine the molecular formula for any compound. Finally, we assume a knowledge of the **Ideal Gas Law**, and the observations from which it is derived.

Goals

Our continuing goal is to relate the properties of the atoms and molecules to the properties of the materials which they comprise. As simple examples, we compare the substances water, carbon dioxide, and nitrogen. Each of these is composed of molecules with few (two or three) atoms and low molecular weight. However, the physical properties of these substances are very different. Carbon dioxide and nitrogen are gases at room temperature, but it is well known that water is a liquid up to 100°C . To liquefy nitrogen, we must cool it to -196°C , so the boiling temperatures of water and nitrogen differ by about 300°C . Water is a liquid over a rather large temperature range, freezing at 0°C . In contrast, nitrogen is a liquid for a very narrow range of temperatures, freezing at -210°C . Carbon dioxide poses yet another very different set of properties. At atmospheric pressure, carbon dioxide gas cannot be liquefied at all: cooling the gas to -60°C converts it directly to solid "dry ice." As is commonly observed, warming dry ice does not produce any liquid, as the solid sublimates directly to gas.

Why should these materials, whose molecules do not seem all that different, behave so differently? What are the important characteristics of these molecules which produce these physical properties? It is important to keep in mind that these are properties of the bulk materials. At this point, it is not even clear that the concept of a molecule is useful in answering these questions about melting or boiling.

There are at least two principal questions that arise about the **Ideal Gas Law**. First, it is interesting to ask whether this law always holds true, or whether there are conditions under which the pressure of the gas cannot be calculated from $\frac{nRT}{V}$. We thus begin by considering the limitations of the validity of the **Ideal Gas Law**. We shall find that the ideal gas law is only approximately accurate and that there are variations which do depend upon the nature of the gas. Second, then, it is interesting to ask why the ideal gas law should ever hold true. In other words, why are the variations not the rule rather than the exception?

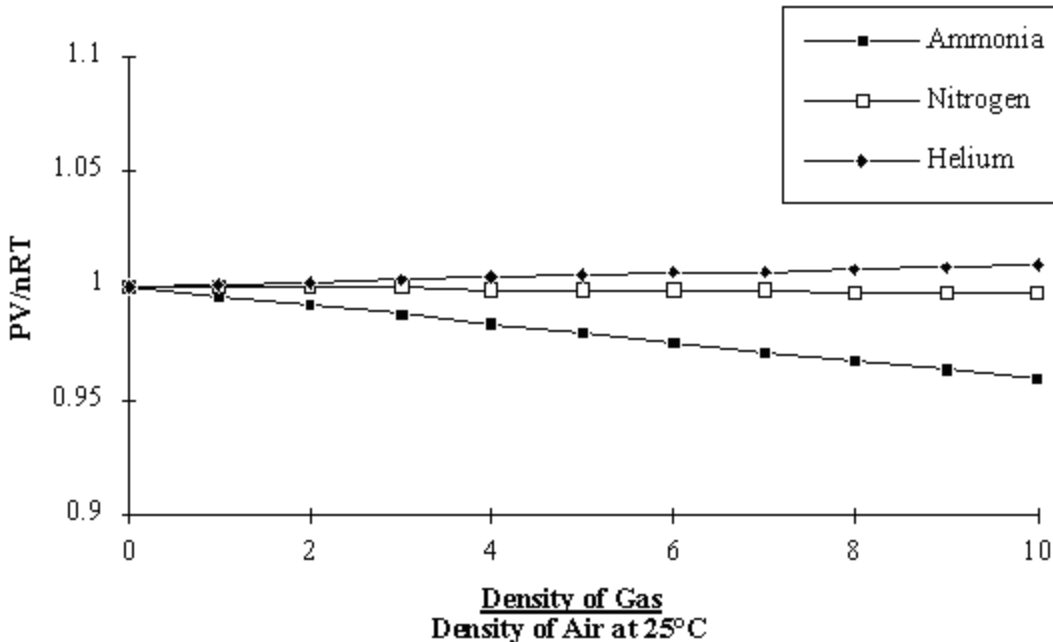
To answer these questions, we need a model which will allow us to relate the properties of bulk materials to the characteristics of individual molecules. We seek to know what happens to a gas when it is compressed into a smaller volume, and why it generates a greater resisting pressure when compressed. Perhaps most fundamentally of all, we seek to know what happens to a substance when it is heated. What property of a gas is measured by the temperature?

Observation 1: Limitations of the Validity of the Ideal Gas Law

To design a systematic test for the validity of the **Ideal Gas Law**, we note that the value of $\frac{PV}{nRT}$, calculated from the observed values of P , V , n , and T , should always be equal to 1, exactly. Deviation of $\frac{PV}{nRT}$ from 1 indicates a violation of the **Ideal Gas Law**. We thus measure the pressure for several gases under a variety of conditions by varying n , V , and T , and we calculate the ratio $\frac{PV}{nRT}$ for these conditions.

[Here](#), the value of this ratio is plotted for several gases as a function of the "particle density" of the gas in moles, $\frac{n}{V}$. To make the analysis of this plot more convenient, the particle density is given in terms of the particle density of an ideal gas at room temperature and atmospheric pressure (i.e. the density of air), which is $0.04087 \frac{\text{mol}}{\text{L}}$. In [this figure](#), a particle density of 10 means that the particle density of the gas is 10 times the particle density of air at room temperature. The x-axis in [the figure](#) is thus unitless.

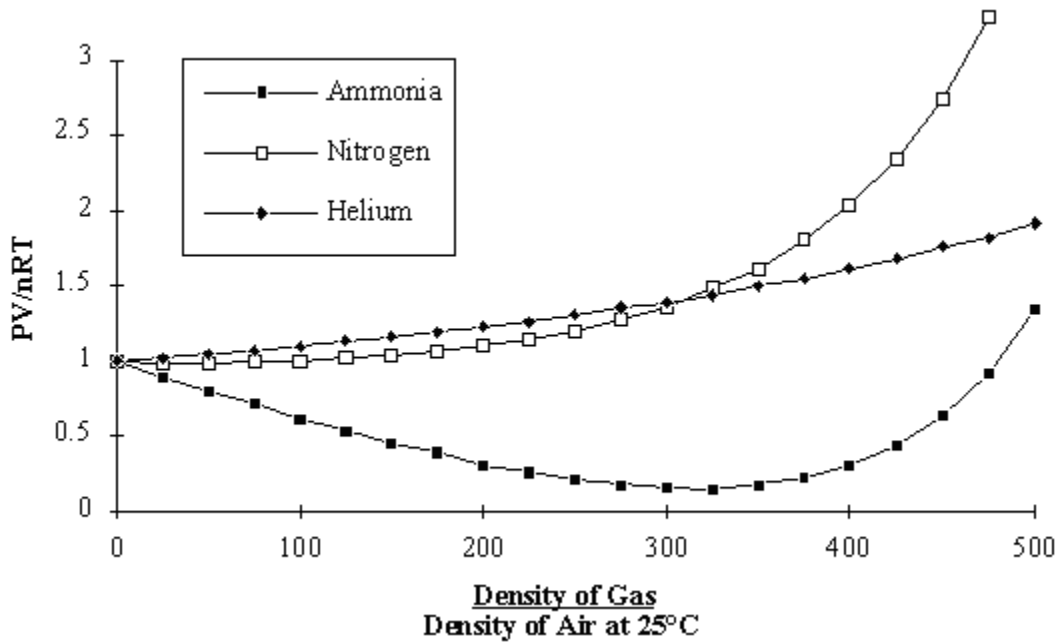
Validity of the Ideal Gas Law



Note that $\frac{PV}{nRT}$ on the y-axis is also unitless and has value exactly 1 for an ideal gas. We observe in the data in [this figure](#) that $\frac{PV}{nRT}$ is extremely close to 1 for particle densities which are close to that of normal air. Therefore, deviations from the **Ideal Gas Law** are not expected under "normal" conditions. This is not surprising, since **Boyle's Law**, **Charles' Law**, and the **Law of Combining Volumes** were all observed under normal conditions. [This figure](#) also shows that, as the particle density increases above the normal range, the value of $\frac{PV}{nRT}$ starts to vary from 1, and the variation depends on the type of gas we are analyzing. However, even for particle densities 10 times greater than that of air at atmospheric pressure, the **Ideal Gas Law** is accurate to a few percent.

Thus, to observe any significant deviations from $PV = nRT$, we need to push the gas conditions to somewhat more extreme values. The results for such extreme conditions are shown [here](#). Note that the densities considered are large numbers corresponding to very high pressures. Under these conditions, we find substantial deviations from the **Ideal Gas Law**. In addition, we see that the pressure of the gas (and thus $\frac{PV}{nRT}$) does depend strongly on which type of gas we are examining. Finally, [this figure](#) shows that deviations from the **Ideal Gas Law** can generate pressures either greater than or less than that predicted by the **Ideal Gas Law**.

Deviations from the Ideal Gas Law



Observation 2: Density and Compressibility of Gas

For low densities for which the **Ideal Gas Law** is valid, the pressure of a gas is independent of the nature of the gas, and is therefore independent of the characteristics of the particles of that gas. We can build on this observation by considering the significance of a low particle density. Even at the high particle densities considered in [this figure](#), all gases have low density in comparison to the densities of liquids. To illustrate, we note that 1 gram of liquid water at its boiling point has a volume very close to 1 milliliter. In comparison, this same 1 gram of water, once evaporated into steam, has a volume of over 1700 milliliters. How does this expansion by a factor of 1700 occur? It is not credible that the individual water molecules suddenly increase in size by this factor. The only plausible conclusion is that the distance between gas molecules has increased dramatically.

Therefore, it is a characteristic of a gas that the molecules are far apart from one another. In addition, the lower the density of the gas the farther apart the molecules must be, since the same number of molecules occupies a larger volume at lower density.

We reinforce this conclusion by noting that liquids and solids are virtually incompressible, whereas gases are easily compressed. This is easily understood if the molecules in a gas are very far apart from one another, in contrast to the liquid and solid where the molecules are so close as to be in contact with one another.

We add this conclusion to the observations in [\[link\]](#) and [\[link\]](#) that the pressure exerted by a gas depends only on the number of particles in the gas and is independent of the type of particles in the gas, provided that the density is low enough. This requires that the gas particles be far enough apart. We conclude that the **Ideal Gas Law** holds true because there is sufficient distance between the gas particles that the identity of the gas particles becomes irrelevant.

Why should this large distance be required? If gas particle A were far enough away from gas particle B that they experience no electrical or magnetic interaction, then it would not matter what types of particles A and B were. Nor would it matter what the sizes of particles A and B were. Finally, then, we conclude from this reasoning that the validity of the ideal gas law rests on the presumption that there are no interactions of any type between gas particles.

Postulates of the Kinetic Molecular Theory

We recall at this point our purpose in these observations. Our primary concern in this study is attempting to relate the properties of individual atoms or molecules to the properties of mass quantities of the materials composed of these atoms or molecules. We now have extensive quantitative observations on some specific properties of gases, and we proceed with the task of relating these to the particles of these gases.

By taking an atomic molecular view of a gas, we can postulate that the pressure observed is a consequence of the collisions of the individual particles of the gas with the walls of the container. This presumes that the gas particles are in constant motion. The pressure is, by definition, the force applied per area, and there can be no other origin for a force on the walls of the container than that provided by the particles themselves. Furthermore,

we observe easily that the pressure exerted by the gas is the same in all directions. Therefore, the gas particles must be moving equally in all directions, implying quite plausibly that the motions of the particles are random.

To calculate the force generated by these collisions, we must know something about the motions of the gas particles so that we know, for example, each particle's velocity upon impact with the wall. This is too much to ask: there are perhaps 10^{20} particles or more, and following the path of each particle is out of the question. Therefore, we seek a model which permits calculation of the pressure without this information.

Based on our observations and deductions, we take as the postulates of our model:

- A gas consists of individual particles in constant and random motion.
- The individual particles have negligible volume.
- The individual particles do not attract or repel one another in any way.
- The pressure of the gas is due entirely to the force of the collisions of the gas particles with the walls of the container.

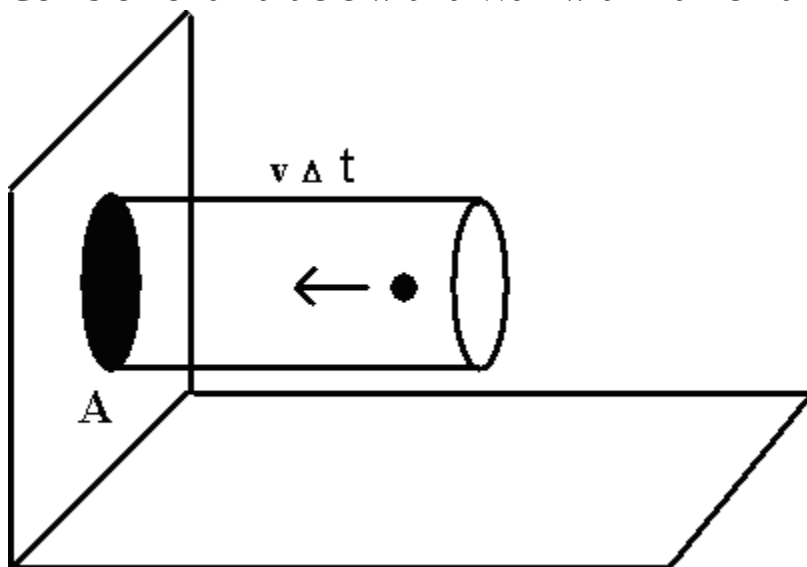
This model is the **Kinetic Molecular Theory of Gases**. We now look to see where this model leads.

Derivation of Boyle's Law from the Kinetic Molecular Theory

To calculate the pressure generated by a gas of N particles contained in a volume V , we must calculate the force F generated per area A by collisions against the walls. To do so, we begin by determining the number of collisions of particles with the walls. The number of collisions we observe depends on how long we wait. Let's measure the pressure for a period of time $\Delta(t)$ and calculate how many collisions occur in that time period. For a particle to collide with the wall within the time $\Delta(t)$, it must start close enough to the wall to impact it in that period of time. If the particle is travelling with speed v , then the particle must be within a distance $v\Delta(t)$ of the wall to hit it. Also, if we are measuring the force exerted on the area A , the particle must hit that area to contribute to our pressure measurement.

For simplicity, we can view the situation pictorially [here](#). We assume that the particles are moving perpendicularly to the walls. (This is clearly not true. However, very importantly, this assumption is only made to simplify the mathematics of our derivation. It is not necessary to make this assumption, and the result is not affected by the assumption.) In order for a particle to hit the area A marked on the wall, it must lie within the cylinder shown, which is of length $v\Delta(t)$ and cross-sectional area A . The volume of this cylinder is $Av\Delta(t)$, so the number of particles contained in the cylinder is $(Av\Delta(t)) \times \frac{N}{V}$.

Collision of a Particle with a Wall within time Δt



Not all of these particles collide with the wall during $\Delta(t)$, though, since most of them are not traveling in the correct direction. There are six directions for a particle to go, corresponding to plus or minus direction in x , y , or z . Therefore, on average, the fraction of particles moving in the correct direction should be $\frac{1}{6}$, assuming as we have that the motions are all random. Therefore, the number of particles which impact the wall in time $\Delta(t)$ is $(Av\Delta(t)) \times \frac{N}{6V}$.

The force generated by these collisions is calculated from Newton's equation, $F = ma$, where a is the acceleration due to the collisions. Consider first a single particle moving directly perpendicular to a wall with velocity v as in [\[link\]](#). We note that, when the particle collides with the

wall, the wall does not move, so the collision must generally conserve the energy of the particle. Then the particle's velocity after the collision must be $-v$, since it is now travelling in the opposite direction. Thus, the change in velocity of the particle in this one collision is $2v$. Multiplying by the number of collisions in $\Delta(t)$ and dividing by the time $\Delta(t)$, we find that the total acceleration (change in velocity per time) is $\frac{2ANv^2}{6V}$, and the force imparted on the wall due collisions is found by multiplying by the mass of the particles:

Equation:

$$F = \frac{2ANmv^2}{6V}$$

To calculate the pressure, we divide by the area A , to find that

Equation:

$$P = \frac{Nmv^2}{3V}$$

or, rearranged for comparison to **Boyle's Law**,

Equation:

$$PV = \frac{Nmv^2}{3}$$

Since we have assumed that the particles travel with constant speed v , then the right side of this equation is a constant. Therefore the product of pressure times volume, PV , is a constant, in agreement with **Boyle's Law**. Furthermore, the product PV is proportional to the number of particles, also in agreement with the **Law of Combining Volumes**. Therefore, the model we have developed to describe an ideal gas is consistent with our experimental observations.

We can draw two very important conclusions from this derivation. First, the inverse relationship observed between pressure and volume and the

independence of this relationship on the type of gas analyzed are both due to the lack of interactions between gas particles. Second, the lack of interactions is in turn due to the great distances between gas particles, a fact which will be true provided that the density of the gas is low.

Interpretation of Temperature

The absence of temperature in the above derivation is notable. The other gas properties have all been incorporated, yet we have derived an equation which omits temperature all together. The problem is that, as we discussed at length above, the temperature was somewhat arbitrarily defined. In fact, it is not precisely clear what has been measured by the temperature. We defined the temperature of a gas in terms of the volume of mercury in a glass tube in contact with the gas. It is perhaps then no wonder that such a quantity does not show up in a mechanical derivation of the gas properties.

On the other hand, the temperature does appear prominently in the **Ideal Gas Law**. Therefore, there must be a greater significance (and less arbitrariness) to the temperature than might have been expected. To discern this significance, we rewrite the last equation above in the form:

Equation:

$$PV = \frac{2}{3}N \left(\frac{1}{2}mv^2 \right)$$

The last quantity in parenthesis can be recognized as the kinetic energy of an individual gas particle, and $N \left(\frac{1}{2}mv^2 \right)$ must be the total kinetic energy (KE) of the gas. Therefore

Equation:

$$PV = \frac{2}{3} \text{KE}$$

Now we insert the **Ideal Gas Law** for PV to find that

Equation:

$$KE = \frac{3}{2}nRT$$

This is an extremely important conclusion, for it reveals the answer to the question of what property is measured by the temperature. We see now that the temperature is a measure of the total kinetic energy of the gas. Thus, when we heat a gas, elevating its temperature, we are increasing the average kinetic energy of the gas particles, causing them to move, on average, more rapidly.

Analysis of Deviations from the Ideal Gas Law

We are at last in a position to understand the observations [above](#) of deviations from the **Ideal Gas Law**. The most important assumption of our model of the behavior of an ideal gas is that the gas molecules do not interact. This allowed us to calculate the force imparted on the wall of the container due to a single particle collision without worrying about where the other particles were. In order for a gas to disobey the **Ideal Gas Law**, the conditions must be such that this assumption is violated.

What do the deviations from ideality tell us about the gas particles? Starting with very low density and increasing the density as in [\[link\]](#), we find that, for many gases, the value of $\frac{PV}{nRT}$ falls below 1. One way to state this result is that, for a given value of V , n , and T , the pressure of the gas is less than it would have been for an ideal gas. This must be the result of the interactions of the gas particles. In order for the pressure to be reduced, the force of the collisions of the particles with the walls must be less than is predicted by our model of an ideal gas. Therefore, the effect of the interactions is to slow the particles as they approach the walls of the container. This means that an individual particle approaching a wall must experience a force acting to pull it back into the body of the gas. Hence, the gas particles must attract one another. Therefore, the effect of increasing the density of the gas is that the gas particles are confined in closer proximity to one another. At this closer range, the attractions of individual particles become significant. It should not be surprising that these attractive forces depend on what the particles are. We note in [\[link\]](#) that deviation from the

Ideal Gas Law is greater for ammonia than for nitrogen, and greater for nitrogen than for helium. Therefore, the attractive interactions of ammonia molecules are greater than those of nitrogen molecules, which are in turn greater than those of helium atoms. We analyze this conclusion in more detail below.

Continuing to increase the density of the gas, we find in [\[link\]](#) that the value of $\frac{PV}{nRT}$ begins to rise, eventually exceeding 1 and continuing to increase. Under these conditions, therefore, the pressure of the gas is greater than we would have expected from our model of non-interacting particles. What does this tell us? The gas particles are interacting in such a way as to increase the force of the collisions of the particles with the walls. This requires that the gas particles repel one another. As we move to higher density, the particles are forced into closer and closer proximity. We can conclude that gas particles at very close range experience strong repulsive forces away from one another.

Our model of the behavior of gases can be summarized as follows: at low density, the gas particles are sufficiently far apart that there are no interactions between them. In this case, the pressure of the gas is independent of the nature of the gas and agrees with the **Ideal Gas Law**. At somewhat higher densities, the particles are closer together and the interaction forces between the particles are attractive. The pressure of the gas now depends on the strength of these interactions and is lower than the value predicted by the **Ideal Gas Law**. At still higher densities, the particles are excessively close together, resulting in repulsive interaction forces. The pressure of the gas under these conditions is higher than the value predicted by the **Ideal Gas Law**.

Observation 3: Boiling Points of simple hydrides

The postulates of the **Kinetic Molecular Theory** provide us a way to understand the relationship between molecular properties and the physical properties of bulk amounts of substance. As a distinct example of such an application, we now examine the boiling points of various compounds, focusing on hydrides of sixteen elements in the main group (Groups IV through VII). These are given [here](#).

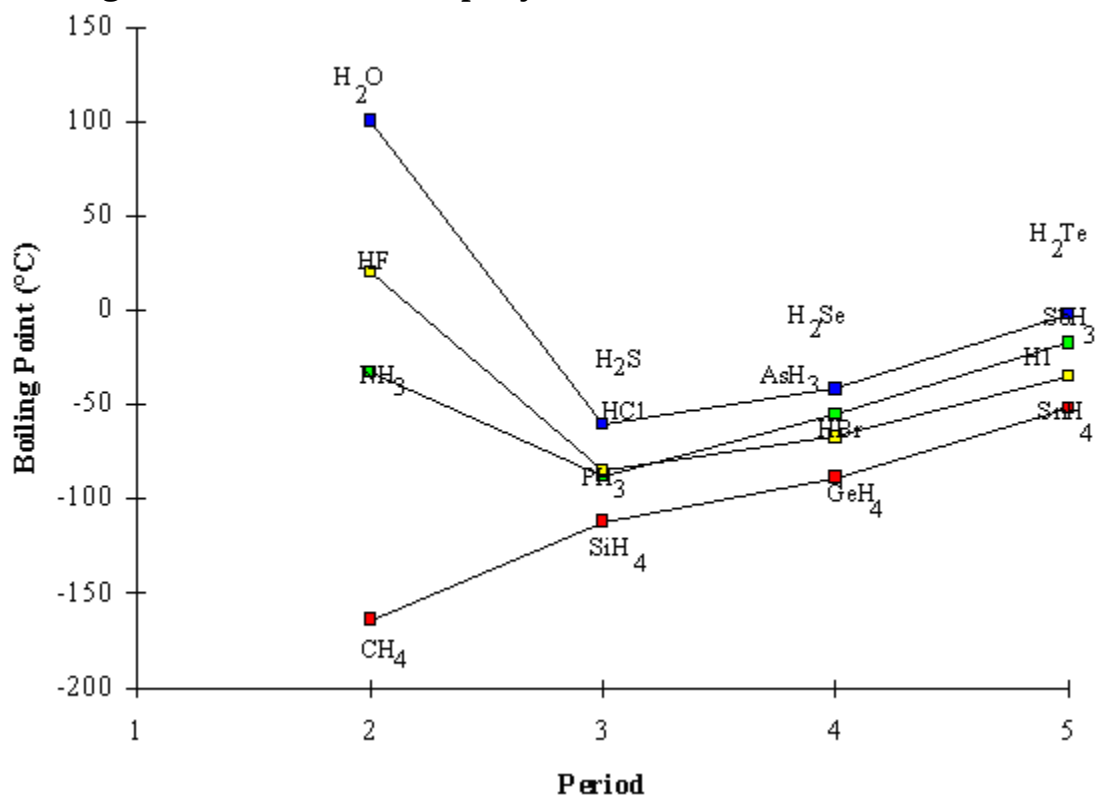
	Boiling Point (°C)
CH_4	-164
NH_3	-33
H_2O	100
HF	20
SiH_4	-111.8
PH_3	-87.7
H_2S	-60.7
HCl	-85
GeH_4	-88.5
AsH_3	-55
H_2Se	-41.5
HBr	-67
SnH_4	-52
SbH_3	-17.1
H_2Te	-2.2
HI	-35

Boiling Points of Hydrides of Groups IV to VII

In tabular form, there are no obvious trends here, and therefore no obvious connection to the structure or bonding in the molecules. The data in [the table](#) are displayed in a suggestive form, however, in [\[link\]](#), the boiling point of each hydride is plotted according to which period (row) of the periodic table the main group element belongs. For example, the Period 2 hydrides (CH_4 , NH_3 , H_2O , and HF) are grouped in a column to the left of the figure, followed by a column for the Period 3 hydrides (SiH_4 , PH_3 , H_2S , HCl), etc.

Now a few trends are more apparent. First, the lowest boiling points in each period are associated with the Group IV hydrides (CH_4 , SiH_4 , GeH_4 , SnH_4), and the highest boiling points in each period belong to the Group VI hydrides (H_2O , H_2S , H_2Se , H_2Te). For this reason, the hydrides belonging to a single group have been connected in [\[link\]](#).

Boiling Points of Main Group Hydrides



Second, we notice that, with the exceptions of NH_3 , H_2O , and HF , the boiling points of the hydrides always increase in a single group as we go down the periodic table: for example, in Group IV, the boiling points increase in the order $CH_4 < SiH_4 < GeH_4 < SnH_4$. Third, we can also

say that the hydrides from Period 2 appear to have unusually high boiling points **except** for CH_4 , which as noted has the lowest boiling point of all.

We begin our analysis of these trends by assuming that there is a relationship between the boiling points of these compounds and the structure and bonding in their molecules. Recalling our kinetic molecular model of gases and liquids, we recognize that a primary difference between these two phases is that the strength of the interaction between the molecules in the liquid is much greater than that in the gas, due to the proximity of the molecules in the liquid. In order for a molecule to leave the liquid phase and enter into the gas phase, it must possess sufficient energy to overcome the interactions it has with other molecules in the liquid. Also recalling the kinetic molecular description, we recognize that, on average, the energies of molecules increase with increasing temperature. We can conclude from these two statements that a high boiling point implies that significant energy is required to overcome intermolecular interactions. Conversely, a substance with a low boiling point must have weak intermolecular interactions, surmountable even at low temperature.

In light of these conclusions, we can now look at [\[link\]](#) as directly (though qualitatively) revealing the comparative strengths of intermolecular interactions of the various hydrides. For example, we can conclude that, amongst the hydrides considered here, the intermolecular interactions are greatest between H_2O molecules and weakest between CH_4 molecules. We examine the three trends in this figure, described above, in light of the strength of intermolecular forces.

First, the most dominant trend in the boiling points is that, within a single group, the boiling points of the hydrides increase as we move **down** the periodic table. This is true in all four groups in [\[link\]](#); the only exceptions to this trend are NH_3 , H_2O , and HF . We can conclude that, with notable exceptions, intermolecular interactions increase with increasing atomic number of the central atom in the molecule. This is true whether the molecules of the group considered have dipole moments (as in Groups V, VI, and VII) or not (as in Group IV). We can infer that the large intermolecular attractions for molecules with large central atoms arises from the large number of charged particles in these molecules.

This type of interaction arises from forces referred to as **London forces** or **dispersion forces**. These forces are believed to arise from the instantaneous interactions of the charged particles from one molecule with the charged particles in an adjacent molecule. Although these molecules may not be polar individually, the nuclei in one molecule may attract the electrons in a second molecule, thus inducing an instantaneous dipole in the second molecule. In turn, the second molecule induces a dipole in the first. Thus, two non-polar molecules can interact as if there were dipole-dipole attractions between them, with positive and negative charges interacting and attracting. The tendency of a molecule to have an induced dipole is called the **polarizability** of the molecule. The more charged particles there are in a molecule, the more **polarizable** a molecule is and the greater the attractions arising from dispersion forces will be.

Second, we note that, without exception, the Group IV hydrides must have the weakest intermolecular interactions in each period. As noted above, these are the only hydrides that have no dipole moment. Consequently, in general, molecules without dipole moments have weaker interactions than molecules which are polar. We must qualify this carefully, however, by noting that the nonpolar $\text{Sn } H_4$ has a higher boiling point than the polar PH_3 and HCl . We can conclude from these comparisons that the increased polarizability of molecules with heavier atoms can offset the lack of a molecular dipole.

Third, and most importantly, we note that the intermolecular attractions involving NH_3 , H_2O , and HF must be uniquely and unexpectedly large, since their boiling points are markedly out of line with those of the rest of their groups. The common feature of these molecules is that they contain small atomic number atoms which are strongly electronegative, which have lone pairs, and which are bonded to hydrogen atoms. Molecules without these features do not have unexpectedly high boiling points. We can deduce from these observations that the hydrogen atoms in each molecule are unusually strongly attracted to the lone pair electrons on the strongly electronegative atoms with the same properties in other molecules. This intermolecular attraction of a hydrogen atom to an electronegative atom is referred to as **hydrogen bonding**. It is clear from our boiling point data that

hydrogen bonding interactions are much stronger than either dispersion forces or dipole-dipole attractions.

Review and Discussion Questions

Exercise:

Problem:

Explain the significance to the development of the kinetic molecular model of the observation that the ideal gas law works well only at low pressure.

Exercise:

Problem:

Explain the significance to the development of the kinetic molecular model of the observation that the pressure predicted by the ideal gas law is independent of the type of gas.

Exercise:

Problem:

Sketch the value of $\frac{PV}{nRT}$ as a function of density for two gases, one with strong intermolecular attractions and one with weak intermolecular attractions but strong repulsions.

Exercise:

Problem:

Give a brief molecular explanation for the observation that the pressure of a gas at fixed temperature increases proportionally with the density of the gas.

Exercise:

Problem:

Give a brief molecular explanation for the observation that the pressure of a gas confined to a fixed volume increases proportionally with the temperature of the gas.

Exercise:

Problem:

Give a brief molecular explanation for the observation that the volume of a balloon increases roughly proportionally with the temperature of the gas inside the balloon.

Exercise:

Problem:

Explain why there is a correlation between high boiling point and strong deviation from the **Ideal Gas Law**.

Exercise:

Problem:

Referring to [\[link\]](#), explain why the hydride of the Group 4 element always has the lowest boiling point in each period.

Exercise:

Problem:

Explain why the Period 2 hydrides except CH_4 all have high boiling points, and explain why CH_4 is an exception.

Phase Equilibrium and Intermolecular Interactions

Foundation

The "phase" of a substance is the particular physical state it is in. The most common phases are solid, liquid, and gas, each easily distinguishable by their significantly different physical properties. A given substance can exist in different phases under different conditions: water can exist as solid ice, liquid, or steam, but water molecules are H_2O regardless of the phase. Furthermore, a substance changes phase without undergoing any chemical transformation: the evaporation of water or the melting of ice occur without decomposition or modification of the water molecules. In describing the differing states of matter changes between them, we will also assume an understanding of the principles of the **Atomic Molecular Theory** and the **Kinetic Molecular Theory**. We will also assume an understanding of the bonding, structure, and properties of individual molecules.

Goals

We have developed a very clear molecular picture of the gas phase, via the Kinetic Molecular Theory. The gas particles (atoms or molecules) are very distant from one another, sufficiently so that there are no interactions between the particles. The path of each particle is independent of the paths of all other particles. We can determine many of the properties of the gas from this description; for example, the pressure can be determined by calculating the average force exerted by collisions of the gas particles with the walls of the container.

To discuss liquids and solids, though, we will be forced to abandon the most fundamental pieces of the Kinetic Molecular Theory of Gases. First, it is clear that the particles in the liquid or solid phases are very much closer together than they are in the gas phase, because the densities of these "condensed" phases are of the order of a thousand times greater than the typical density of a gas. In fact, we should expect that the particles in the liquid or solid phases are essentially in contact with each other constantly. Second, since the particles in liquid or solid are in close contact, it is not reasonable to imagine that the particles do not interact with one another. Our

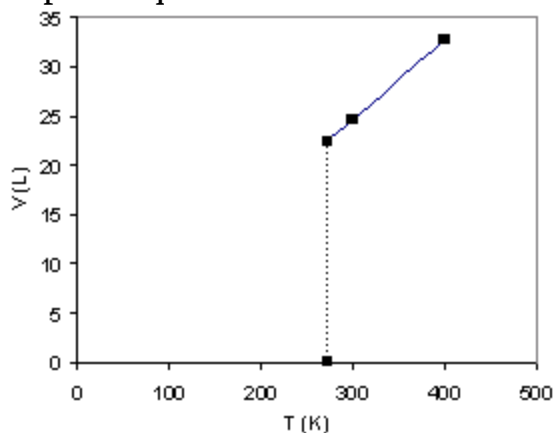
assumption that the gas particles do not interact is based, in part, on the concept that the particles are too far apart to interact. Moreover, particles in a liquid or solid must interact, for without attractions between these particles, random motion would require that the solid or liquid dissipate or fall apart.

In this study, we will pursue a model to describe the differences between condensed phases and gases and to describe the transitions which occur between the solid, liquid, and gas phases. We will find that intermolecular interactions play the most important role in governing phase transitions, and we will pursue an understanding of the variations of these intermolecular interactions for different substances.

Observation 1: Gas-Liquid Phase Transitions

We begin by returning to our observations of **Charles' Law**. Recall that we trap an amount of gas in a cylinder fitted with a piston, and we apply a fixed pressure to the piston. We vary the temperature of the gas, and since the pressure applied to the piston is constant, the piston moves to maintain a constant pressure of the trapped gas. At each temperature, we then measure the volume of the gas. From our previous observations, we know that the volume of the gas is proportional to the absolute temperature in degrees Kelvin. Thus a graph of [volume versus absolute temperature](#) is a straight line, which can be extrapolated to zero volume at 0K.

Vapor-Liquid Phase Transition

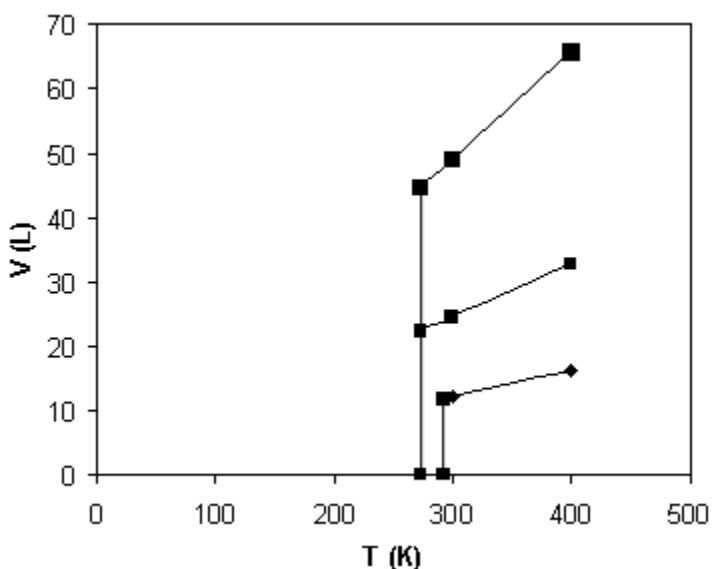


Consider, then, trying to measure the volume for lower and lower temperatures to follow [the graph](#). To be specific, we take exactly 1.00 mol of butane C_4H_{10} at 1 atm pressure. As we lower the temperature from 400K to 300K, we observe the expected proportional decrease in the volume from 32.8L to 24.6L and this proportionality works very well for temperatures just slightly above 272.6K, where the volume is 22.4L. However, when we reach 272.6K, the volume of the butane drops very abruptly, falling to about 0.097L at temperatures just slightly below 272.6K. This is less than one-half of one percent of the previous volume! The striking change in volume is shown in [the graph](#) as a vertical line at 272.6K.

This dramatic change in physical properties at one temperature is referred to as a **phase transition**. When cooling butane through the temperature 272.6K, the butane is abruptly converted at that temperature from one phase, gas, to another phase, liquid, with very different physical properties. If we reverse the process, starting with liquid butane at 1 atm pressure and temperature below 272.6K and then heating, we find that the butane remains entirely liquid for temperatures below 272.6K and then becomes entirely gas for temperatures above 272.6K. We refer to the temperature of the phase transition as the **boiling point** temperature. (We will discuss the phases present **at** the boiling point, rather than above and below that temperature, in [another section](#).)

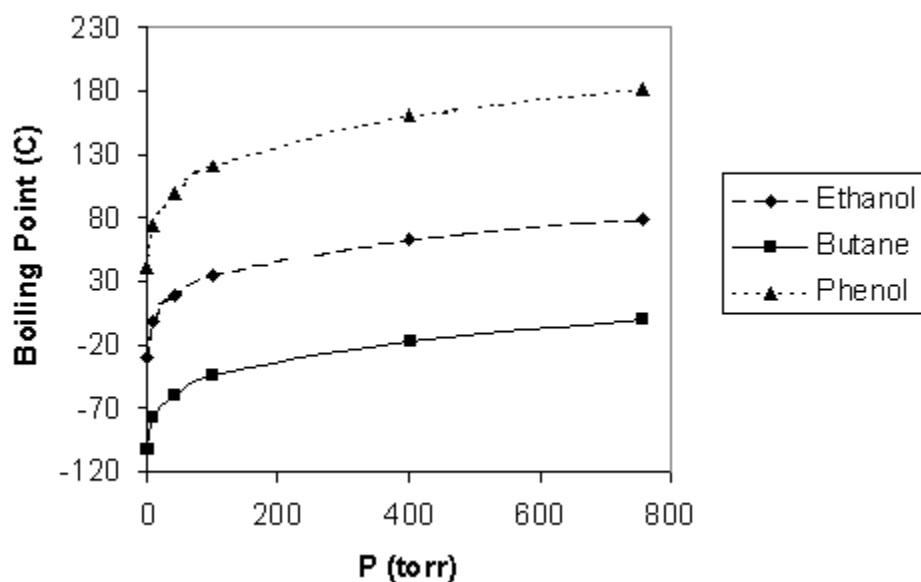
We now consider how the phase transition depends on a variety of factors. First, we consider capturing 2.00 mol of butane in the cylinder initially, still at 1 atm pressure. The volume of 2.00 mol is twice that of 1.00 mol, by **Avogadro's hypothesis**. The proportional decrease in the volume of 2.00 mol of gas is shown in [\[link\]](#) along with the previous result for 1.00 mol. Note that the phase transition is observed to occur at exactly the same temperature, 272.6K, even though there is double the mass of butane.

Variation of Phase Transition with Pressure



Consider instead then varying the applied pressure. The result for cooling 1.00 mol of butane at a constant 2.00 atm pressure is also shown in [\[link\]](#). We observe the now familiar phase transition with a similar dramatic drop in volume. However, in this case, we find that the phase transition occurs at 293.2K, over 20K higher than at the lower pressure. Therefore, the temperature of the phase transition depends on the pressure applied. We can measure the boiling point temperature of butane as a function of the applied pressure, and this result is plotted [here](#).

Boiling Point versus Pressure



Finally, we consider varying the substance which we trap in the cylinder. In each case, we discover that the boiling point temperature depends on both what the substance is and on the applied pressure, but does not depend on the amount of the substance we trap. In [\[link\]](#), we have also plotted the boiling point as a function of the pressure for several substances. It is very clear that the boiling points for different substances can be very different from one another, although the variation of the boiling point with pressure looks similar from one substance to the next.

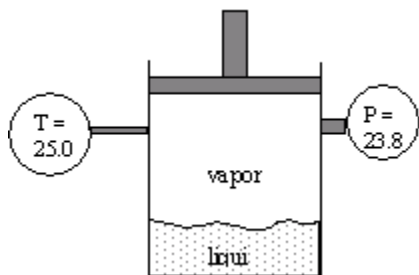
Observation 2: Vapor pressure of a liquid

Our previous observations indicate that, for a given pressure, there is a phase transition temperature for liquid and gas: below the boiling point, the liquid is the only **stable** phase which exists, and any gas which might exist at that point will spontaneously condense into liquid. Above the boiling point, the gas is the only stable phase.

However, we can also commonly observe that any liquid left in an open container will, under most conditions, eventually evaporate, even if the temperature of the liquid is well below the normal boiling point. For example, we often observe that liquid water evaporates at temperatures well below the boiling point. This observation only seems surprising in light of the discussion of above. Why would liquid water spontaneously evaporate if liquid is the more stable phase below the boiling point? We clearly need to further develop our understanding of phase transitions.

The tendency of a liquid to evaporate is referred to as its **volatility**: a more volatile liquid evaporates more readily. To make a quantitative measure of liquid volatility, we slightly modify our previous cylinder-piston apparatus by adding a gauge to measure the pressure of gas inside the cylinder. ([Here](#) is an illustration.) We begin with liquid water only in the cylinder with an applied pressure of 1 atm at a temperature of 25°C. We now pull back the piston by an arbitrary amount, and then we lock the piston in place, fixing the volume trapped inside the cylinder. We might expect to have created a vacuum in the cavity above the liquid water, and as such we might expect that the pressure inside the cylinder is small or zero.

Measuring Vapor Pressure



Although there was initially no gas in the container, we observe that the pressure inside the container rises to a fixed value of 23.8 torr. Clearly, the observation of pressure indicates the presence of gaseous water inside the container, arising from evaporation of some, but not all, of the liquid water. Therefore, some of the liquid water must have evaporated. On the other hand, a look inside the container reveals that there is still liquid water present. Since both a liquid phase and a gas phase are present at the same time, we say that the liquid water and the water vapor must be in **phase equilibrium**. The term **equilibrium** in this case indicates that neither the vapor nor the liquid spontaneously converts into the other phase. Rather, both phases are stable at equilibrium.

Very interestingly, we can repeat this measurement by pulling the piston back to any other arbitrary position before locking it down, and, provided that there is still some liquid water present, the pressure in the container in every case rises to the same fixed value of 23.8 torr. It does not matter what volume we have trapped inside the cylinder, nor does it matter how much liquid water we started with. As long as there is still some liquid water present in the cylinder at equilibrium, the pressure of the vapor above that liquid is 23.8 torr at 25°C.

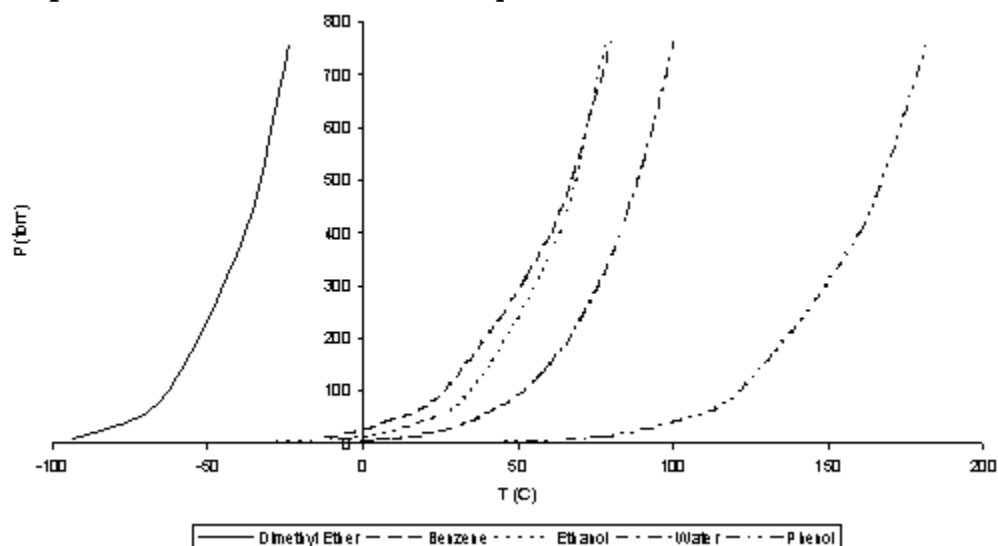
Note that, in varying either the amount of liquid initially or the fixed volume of the container, the **amount** of liquid water that evaporates must be different in each case. This can be seen from the fact that the volume available for vapor must be different in varying either the volume of the container or the initial volume of the liquid. Since we observe that the pressure of the vapor is the same at a fixed temperature, the differing volumes reveal differing numbers of moles of water vapor. Clearly it is the **pressure** of the vapor, not the amount, which is the most important property in establishing the equilibrium between the liquid and the vapor. We can

conclude that, at a given fixed temperature, there is a single specific pressure at which a given liquid and its vapor will be in phase equilibrium. We call this the **vapor pressure** of the liquid.

We can immediately observe some important features of the vapor pressure. First, for a given substance, the vapor pressure varies with the temperature. This can be found by simply increasing the temperature on the closed container in the preceding experiment. In every case, we observe that the equilibrium vapor pressure increases with increases in the temperature.

The vapor pressures of several liquids at several temperatures are shown [here](#). The vapor pressure for each liquid increases smoothly with the temperature, although the relationship between vapor pressure and temperature is definitely not proportional.

Vapor Pressures of Various Liquids



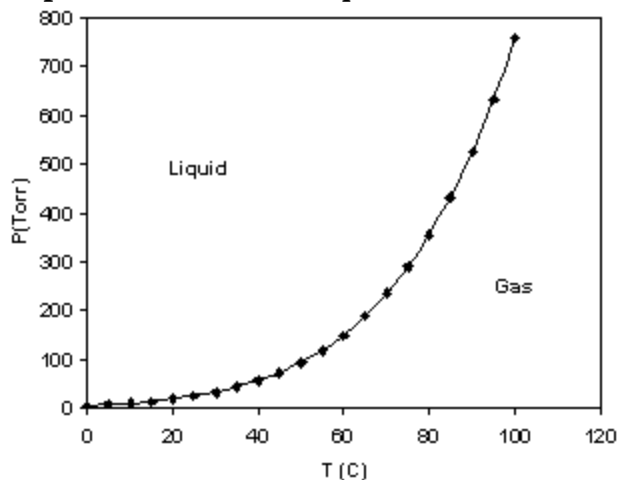
Second, [link](#) clearly illustrates that the vapor pressure depends strongly on what the liquid substance is. These variations reflect the differing **volatilities** of the liquids: those with higher vapor pressures are more volatile. In addition, there is a very interesting correlation between the volatility of a liquid and the boiling point of the liquid. Without exception, the substances with high boiling points have low vapor pressures and vice versa.

Looking more closely at the connection between boiling point and vapor pressure, we can find an important relationship. Looking at [\[link\]](#), we discover that the vapor pressure of each liquid is equal to 760 torr (which is equal to 1 atm) at the boiling point for that liquid. How should we interpret this? At an applied pressure of 1 atm, the temperature of the phase transition from liquid to gas is the temperature at which the vapor pressure of the liquid is equal to 1 atm. This statement is actually true regardless of which pressure we consider: if we apply a pressure of 0.9 atm, the boiling point temperature is the temperature at which the liquid has a vapor pressure of 0.9 atm. Stated generally, the liquid undergoes phase transition at the temperature where the vapor pressure equals the applied pressure.

Observation 3: Phase Diagrams

Since the boiling point is the temperature at which the applied pressure equals the vapor pressure, then we can view [\[link\]](#) in a different way. Consider the specific case of water, with vapor pressure given [here](#). To find the boiling point temperature at 1 atm pressure, we need to find the temperature at which the vapor pressure is 1 atm. To do so, we find the point on the graph where the vapor pressure is 1 atm and read off the corresponding temperature, which must be the boiling point. This will work at any given pressure. Viewed this way, for water [\[link\]](#) gives us **both** the vapor pressure as a function of the temperature **and** the boiling point temperature as a function of the pressure. They are the same graph.

Vapor Pressure of Liquid Water



Recall that, at the boiling point, we observe that both liquid and gas are at equilibrium with one another. This is true at every combination of applied pressure and boiling point temperature. Therefore, for every combination of temperature and pressure on the graph in [\[link\]](#), we observe liquid-gas equilibrium.

What happens at temperature/pressure combinations which are not on the line in [\[link\]](#)? To find out, we first start at a temperature-pressure combination on the graph and elevate the temperature. The vapor pressure of the liquid rises, and if the applied pressure does not also increase, then the vapor pressure will be greater than the applied pressure. We must therefore not be at equilibrium anymore. All of the liquid vaporizes, and there is only gas in the container. Conversely, if we start at a point on the graph and lower the temperature, the vapor pressure is below the applied pressure, and we observe that all of the gas condenses into the liquid.

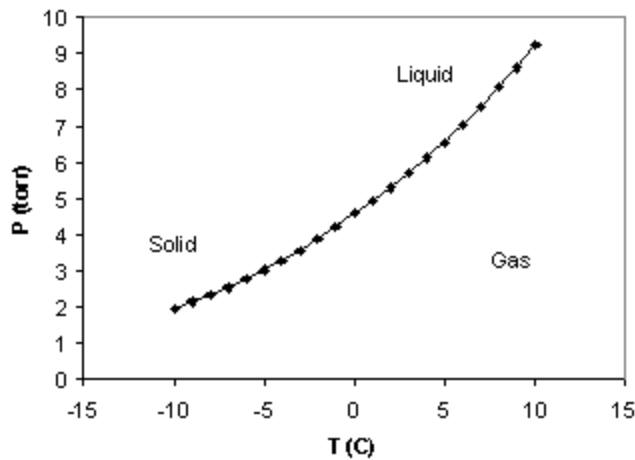
Now, what if we start at a temperature-pressure combination on the graph and elevate the applied pressure without raising the temperature? The applied pressure will be greater than the vapor pressure, and all of the gas will condense into the liquid. [\[link\]](#) thus actually reveals to us what phase or phases are present at each combination of temperature and pressure: along the line, liquid and gas are in equilibrium; above the line, only liquid is present; below the line, only gas is present. When we label the graph with the phase or phases present in each region as in [\[link\]](#), we refer to the graph as a **phase diagram**.

Of course, [\[link\]](#) only includes liquid, gas, and liquid-gas equilibrium. We know that, if the temperature is low enough, we expect that the water will freeze into solid. To complete the phase diagram, we need additional observations.

We go back to our apparatus in [\[link\]](#) and we establish liquid-gas water phase equilibrium at a temperature of 25°C and 23.8 torr. If we slowly lower the temperature, the vapor pressure decreases slowly as well, as shown in [\[link\]](#). If we continue to lower the temperature, though, we observe an interesting transition, as shown in the more detailed [\[link\]](#). The very smooth variation in the vapor pressure shows a slight, almost

unnoticeable break very near to 0°C . Below this temperature, the pressure continues to vary smoothly, but along a slightly different curve.

Water Phase Transitions

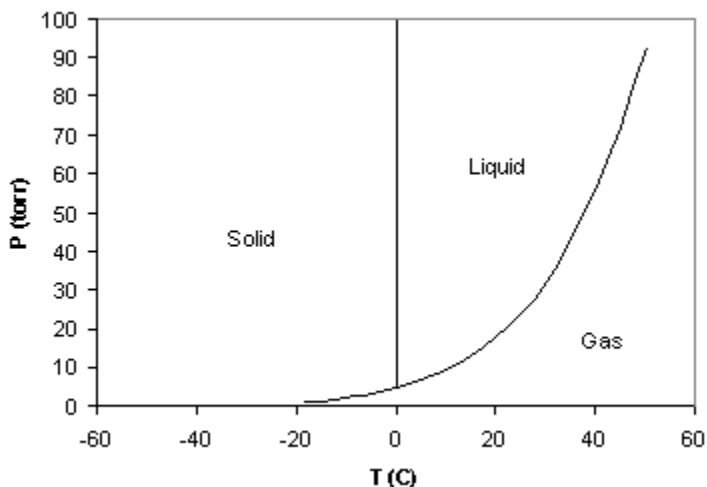


To understand what we have observed, we examine the contents of the container. We find that, at temperatures below 0°C , the water in the container is now an equilibrium mixture of water vapor and solid water (ice), and there is no liquid present. The direct transition from solid to gas, without liquid, is called **sublimation**. For pressure-temperature combinations along this new curve below 0°C , then, the curve shows the solid-gas equilibrium conditions. As before, we can interpret this two ways. The solid-gas curve gives the vapor pressure of the solid water as a function of temperature, and also gives the sublimation temperature as a function of applied pressure.

[\[link\]](#) is still not a complete phase diagram, because we have not included the combinations of temperature and pressure at which solid and liquid are at equilibrium. As a starting point for these observations, we look more carefully at the conditions near 0°C . Very careful measurements reveal that the solid-gas line and the liquid-gas line intersect in [\[link\]](#) where the temperature is 0.01°C . Under these conditions, we observe inside the container that solid, liquid, and gas are all three at equilibrium inside the container. As such, this unique temperature-pressure combination is called the **triple point**. At this point, the liquid and the solid have the same vapor pressure, so all three phases can be at equilibrium. If we raise the applied pressure slightly above the triple point, the vapor must disappear. We can observe that, by very slightly varying the temperature, the solid and liquid

remain in equilibrium. We can further observe that the temperature at which the solid and liquid are in equilibrium varies almost imperceptibly as we increase the pressure. If we include the solid-liquid equilibrium conditions on the previous phase diagram, we get [this](#), where the solid-liquid line is very nearly vertical.

Phase Diagram of Water



Each substance has its own unique phase diagram, corresponding to the diagram in [\[link\]](#) for water.

Observation 4: Dynamic Equilibrium

There are several questions raised by our observations of phase equilibrium and vapor pressure. The first we will consider is why the pressure of a vapor in equilibrium with its liquid does not depend on the volume of the container into which the liquid evaporates, or on the amount of liquid in the container, or on the amount of vapor in the container. Why do we get the same pressure for the same temperature, regardless of other conditions? To address this question, we need to understand the coexistence of vapor and liquid in equilibrium. How is this equilibrium achieved?

To approach these questions, let us look again at the situation in [\[link\]](#). We begin with a container with a fixed volume containing some liquid, and equilibrium is achieved at the vapor pressure of the liquid at the fixed temperature given. When we adjust the volume to a larger fixed volume, the pressure adjusts to equilibrium at exactly the same vapor pressure.

Clearly, there are more molecules in the vapor after the volume is increased and equilibrium is reestablished, because the vapor exerts the same pressure in a larger container at the same temperature. Also clearly, more liquid must have evaporated to achieve this equilibrium. A very interesting question to pose here is how the liquid responded to the increase in volume, which presumably only affected the space in which the gas molecules move. How did the liquid "know" to evaporate when the volume was increased? The molecules in the liquid could not detect the increase in volume for the gas, and thus could not possibly be responding to that increase.

The only reasonable conclusion is that the molecules in the liquid were always evaporating, even before the volume of the container was increased. There must be a constant movement of molecules from the liquid phase into the gas phase. Since the pressure of the gas above the liquid remains constant when the volume is constant, then there must be a constant number of molecules in the gas. If evaporation is constantly occurring, then condensation must also be occurring constantly, and molecules in the gas must constantly be entering the liquid phase. Since the pressure remains constant in a fixed volume, then the number of molecules entering the gas from the liquid must be exactly offset by the number of molecules entering the liquid from the gas.

At equilibrium, therefore, the pressure and temperature inside the container are unchanging, but there is constant movement of molecules between the phases. This is called **dynamic equilibrium**. The situation is "equilibrium" in that the observable properties of the liquid and gas in the container are not changing, but the situation is "dynamic" in that there is constant movement of molecules between phases. The dynamic processes that take place offset each other exactly, so that the properties of the liquid and gas do not change.

What happens when we increase the volume of the container to a larger fixed volume? We know that the pressure equilibrates at the same vapor pressure, and that therefore there are more molecules in the vapor phase. How did they get there? It must be the case that when the volume is increased, evaporation initially occurs more rapidly than condensation until equilibrium is achieved. The rate of evaporation must be determined by the

number of molecules in the liquid which have sufficient kinetic energy to escape the intermolecular forces in the liquid, and according to the kinetic molecular theory, this number depends only on the temperature, not on the volume. However, the rate of condensation must depend on the frequency of molecules striking the surface of the liquid. According to the Kinetic Molecular Theory, this frequency must decrease when the volume is increased, because the density of molecules in the gas decreases. Therefore, the rate of condensation becomes smaller than the rate of evaporation when the volume is increased, and therefore there is a net flow of molecules from liquid to gas. This continues until the density of molecules in the gas is restored to its original value, at which point the rate of evaporation is matched by the rate of condensation. At this point, this pressure stops increasing and is the same as it was before the volume was increased.

Review and Discussion Questions

Exercise:

Problem:

In the phase diagram for water in [\[link\]](#), start at the point where the temperature is 60°C and the pressure is 400 torr. Slowly increase the temperature with constant pressure until the temperature is 100°C. State what happens physically to the water during this heating process.

Exercise:

Problem:

In the phase diagram for water in [\[link\]](#), start at the point where the temperature is 60°C and the pressure is 400 torr. Slowly lower the pressure at constant temperature until the pressure is 80 torr. State what happens physically to the water during this process.

Exercise:

Problem:

Explain why [\[link\]](#) is both a graph of the boiling point of liquid water as a function of applied pressure and a graph of the vapor pressure of liquid water as a function of temperature.

Exercise:**Problem:**

We observe that, when the applied pressure is less than the vapor pressure of a liquid, all of the liquid will spontaneously evaporate. In terms of dynamic equilibrium, explain why no liquid can be present under these conditions.

Exercise:**Problem:**

Using arguments from the Kinetic Molecular Theory and the concept of dynamic equilibrium, explain why, at a given applied pressure, there can be one and only one temperature, the boiling point, at which a specific liquid and its vapor can be in equilibrium.

Exercise:**Problem:**

Using dynamic equilibrium arguments, explain why the vapor pressure of a liquid is independent of the amount of liquid present.

Exercise:**Problem:**

Using dynamic equilibrium arguments, explain why the vapor pressure of a liquid is independent of the volume available for the vapor above the liquid.

Exercise:

Problem:

Using dynamic equilibrium arguments, explain why a substance with weaker intermolecular forces has a greater vapor pressure than one with stronger intermolecular forces.

Exercise:**Problem:**

According to [\[link\]](#) the vapor pressure of phenol is much less than the vapor pressure of dimethyl ether. Which of these substances has the greater intermolecular attractions? Which substance has the higher boiling point? Explain the difference in the intermolecular attractions in terms of molecular structure.

Exercise:**Problem:**

The text describes dynamic equilibrium between a liquid and its vapor at the boiling point. Describe the dynamic equilibrium between a liquid and its solid at the melting point. Using this description, explain why the melting point of a solid varies very little as the pressure increases.

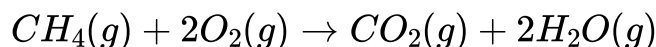
Reaction Equilibrium in the Gas Phase

Foundation

In beginning our study of the reactions of gases, we will assume a knowledge of the physical properties of gases as described by the **Ideal Gas Law** and an understanding of these properties as given by the postulates and conclusions of the **Kinetic Molecular Theory**. We assume that we have developed a dynamic model of phase equilibrium in terms of competing rates. We will also assume an understanding of the bonding, structure, and properties of individual molecules.

Goals

In performing stoichiometric calculations, we assume that we can calculate the amount of product of a reaction from the amount of the reactants we start with. For example, if we burn methane gas, $CH_4(g)$, in excess oxygen, the reaction **Equation:**



occurs, and the number of moles of $CO_2(g)$ produced is assumed to equal the number of moles of $CH_4(g)$ we start with.

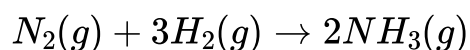
From our study of phase transitions we have learned the concept of equilibrium. We observed that, in the transition from one phase to another for a substance, under certain conditions both phases are found to coexist, and we refer to this as phase equilibrium. It should not surprise us that these same concepts of equilibrium apply to chemical reactions as well. In the [reaction](#), therefore, we should examine whether the reaction actually produces exactly one mole of CO_2 for every mole of CH_4 we start with or whether we wind up with an equilibrium mixture containing both CO_2 and CH_4 . We will find that different reactions provide us with varying answers. In many cases, virtually all reactants are consumed, producing the stoichiometric amount of product. However, in many other cases, substantial amounts of reactant are still present when the reaction achieves equilibrium, and in other cases, almost no product is produced at equilibrium. Our goal will be to understand, describe and predict the reaction equilibrium.

An important corollary to this goal is to attempt to control the equilibrium. We will find that varying the conditions under which the reaction occurs can vary the amounts of reactants and products present at equilibrium. We will develop a general principle for predicting how the reaction conditions affect the amount of product produced at equilibrium.

Observation 1: Reaction equilibrium

We begin by analyzing a significant industrial chemical process, the synthesis of ammonia gas, NH_3 , from nitrogen and hydrogen:

Equation:

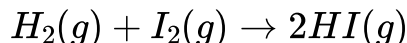


If we start with 1 mole of N_2 and 3 moles of H_2 , the balanced equation predicts that we will produce 2 moles of NH_3 . In fact, if we carry out this reaction starting with these quantities of nitrogen and hydrogen at 298K in a 100.0L reaction vessel, we observe that the number of moles of NH_3 produced is 1.91 mol. This "yield" is less than predicted by the balanced equation, but the difference is not due to a limiting reagent factor. Recall that, in stoichiometry, the limiting reagent is the one that is present in less than the ratio of moles given by the balanced equation. In this case, neither N_2 nor H_2 is limiting because they are present initially in a 1:3 ratio, exactly matching the stoichiometry. Note also that this seeming deficit in the yield is not due to any experimental error or imperfection, nor is it due to poor measurements or preparation. Rather, the observation that, at 298K, 1.91 moles rather than 2 moles are produced is completely reproducible: every measurement of this reaction at this temperature in this volume starting with 1 mole of N_2 and 3 moles of H_2 gives this result. We conclude that the [reaction](#) achieves **reaction equilibrium** in which all three gases are present in the gas mixture. We can determine the amounts of each gas at equilibrium from the stoichiometry of the reaction. When $n_{NH_3} = 1.91$ mol are created, the number of moles of N_2 remaining at equilibrium is $n_{N_2} = 0.045$ mol and $n_{H_2} = 0.135$ mol.

It is important to note that we can vary the relative amount of NH_3 produced by varying the temperature of the reaction, the volume of the vessel in which the reaction occurs, or the relative starting amounts of N_2 and H_2 . We shall study and analyze this observation in detail in later sections. For now, though, we demonstrate that the concept of reaction equilibrium is general to all reactions.

Consider the reaction

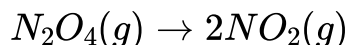
Equation:



If we begin with 1.00 mole of H_2 and 1.00 mole of I_2 at 500K in a reaction vessel of fixed volume, we observe that, at equilibrium, $n_{HI} = 1.72$ mol, leaving in the equilibrium mixture $n_{H_2} = 0.14$ mol and $n_{I_2} = 0.14$ mol.

Similarly, consider the decomposition reaction

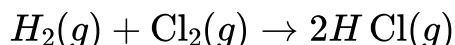
Equation:



At 298K in a 100.0L reaction flask, 1.00 mol of N_2O_4 partially decomposes to produce, at equilibrium, $n_{NO_2} = 0.64$ mol and $n_{N_2O_4} = 0.68$ mol.

Some chemical reactions achieve an equilibrium that appears to be very nearly complete reaction. For example,

Equation:



If we begin with 1.00 mole of H_2 and 1.00 mole of Cl_2 at 298K in a reaction vessel of fixed volume, we observe that, at equilibrium, n_{HCl} is almost exactly 2.00 mol, leaving virtually no H_2 or Cl_2 . This does not mean that the reaction has not come to equilibrium. It means instead that, at equilibrium, there are essentially no reactants remaining.

In each of these cases, the amounts of reactants and products present at equilibrium vary as the conditions are varied but are completely reproducible for fixed conditions. Before making further observations that will lead to a quantitative description of the reaction equilibrium, we consider a qualitative description of equilibrium.

We begin with a dynamic equilibrium description. We know from our studies of phase transitions that equilibrium occurs when the rate of the forward process (e.g. evaporation) is matched by the rate of reverse process (e.g. condensation). Since we have now observed that gas reactions also come to equilibrium, we postulate

that at equilibrium the forward reaction rate is equal to the reverse reaction rate. For example, in the reaction [here](#), the rate of decomposition of N_2O_4 molecules at equilibrium must be exactly matched by the rate of recombination (or **dimerization**) of NO_2 molecules.

To show that the forward and reverse reactions continue to happen at equilibrium, we start with the NO_2 and N_2O_4 mixture at equilibrium and we vary the volume of the flask containing the mixture. We observe that, if we increase the volume and the reaction is allowed to come to equilibrium, the amount of NO_2 at equilibrium is larger at the expense of a smaller amount of N_2O_4 . We can certainly conclude that the amounts of the gases at equilibrium depend on the reaction conditions. However, if the forward and reverse reactions stop once the equilibrium amounts of material are achieved, the molecules would not "know" that the volume of the container had increased. Since the reaction equilibrium can and does respond to a change in volume, it must be that the change in volume affects the rates of both the forward and reverse processes. This means that both reactions must be occurring at equilibrium, and that their rates must exactly match at equilibrium.

This reasoning reveals that the amounts of reactant and product present at equilibrium are determined by the rates of the forward and reverse reactions. If the rate of the forward reaction (e.g. decomposition of N_2O_4) is faster than the rate of the reverse reaction, then at equilibrium we have more product than reactant. If that difference in rates is very large, at equilibrium there will be much more product than reactant. Of course, the converse of these conclusions is also true. It must also be the case that the rates of these processes depends on, amongst other factors, the volume of the reaction flask, since the amounts of each gas present at equilibrium change when the volume is changed.

Observation 2: Equilibrium constants

It was noted above that the equilibrium partial pressures of the gases in a reaction vary depending upon a variety of conditions. These include changes in the initial numbers of moles of reactants and products, changes in the volume of the reaction flask, and changes in the temperature. We now study these variations quantitatively.

Consider first the reaction [here](#). Following on our previous study of this reaction, we inject an initial amount of $N_2O_4(g)$ into a 100L reaction flask at 298K. Now, however, we vary the initial number of moles of $N_2O_4(g)$ in the flask and measure

the equilibrium pressures of both the reactant and product gases. The results of a number of such studies are given [here](#).

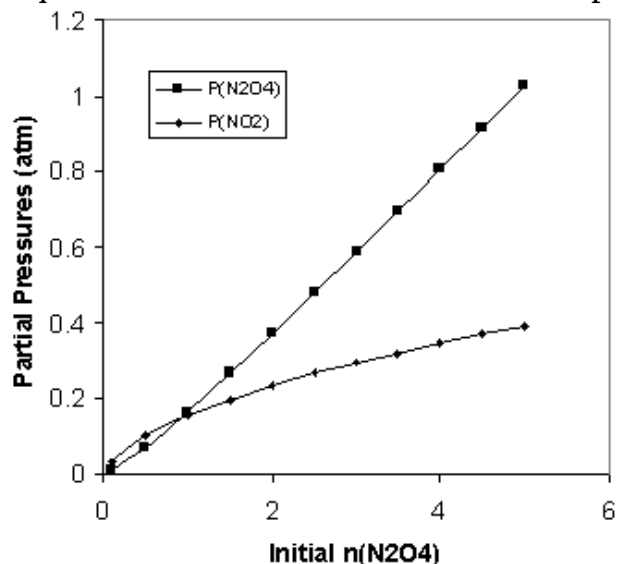
Initial $n_{N_2O_4}$	$P_{N_2O_4}$ (atm)	P_{NO_2} (atm)
0.1	0.00764	0.033627
0.5	0.071011	0.102517
1	0.166136	0.156806
1.5	0.26735	0.198917
2	0.371791	0.234574
2.5	0.478315	0.266065
3	0.586327	0.294578
3.5	0.695472	0.320827
4	0.805517	0.345277
4.5	0.916297	0.368255
5	1.027695	0.389998

Equilibrium Partial Pressures in Decomposition Reaction

We might have expected that the amount of NO_2 produced at equilibrium would increase in direct proportion to increases in the amount of N_2O_4 we begin with. [\[link\]](#) shows that this is not the case. Note that when we increase the initial amount of N_2O_4 by a factor of 10 from 0.5 moles to 5.0 moles, the pressure of NO_2 at equilibrium increases by a factor of less than 4.

The relationship between the pressures at equilibrium and the initial amount of N_2O_4 is perhaps more easily seen in a graph of the data in [\[link\]](#), as shown in [\[link\]](#). There are some interesting features here. Note that, when the initial amount of N_2O_4 is less than 1 mol, the equilibrium pressure of NO_2 is greater than that of N_2O_4 . These relative pressures reverse as the initial amount increases, as the N_2O_4 equilibrium pressure keeps track with the initial amount but the NO_2 pressure falls short. Clearly, the equilibrium pressure of NO_2 does not increase proportionally with the initial amount of N_2O_4 . In fact, the increase is slower than proportionality, suggesting perhaps a square root relationship between the pressure of NO_2 and the initial amount of N_2O_4 .

Equilibrium Partial Pressures in Decomposition Reaction



We test this in [\[link\]](#) by plotting P_{NO_2} at equilibrium versus the square root of the initial number of moles of N_2O_4 . [\[link\]](#) makes it clear that this is not a simple proportional relationship, but it is closer. Note in [\[link\]](#) that the equilibrium pressure $P_{N_2O_4}$ increases close to proportionally with the initial amount of N_2O_4 . This suggests plotting P_{NO_2} versus the square root of $P_{N_2O_4}$. This is done in [\[link\]](#), where we discover that there is a very simple proportional relationship between the variables plotted in this way. We have thus observed that

Equation:

$$P_{NO_2} = c\sqrt{2P_{N_2O_4}}$$

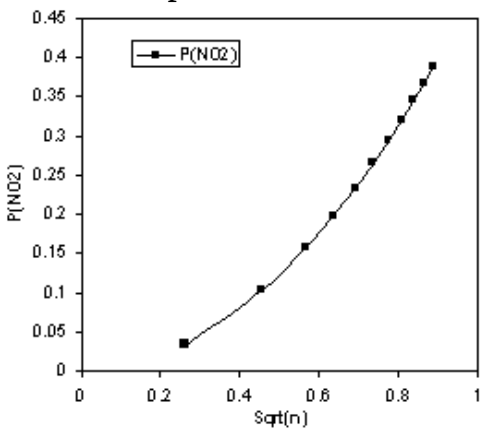
where c is the slope of the graph. [\[link\]](#) can be rewritten in a standard form

Equation:

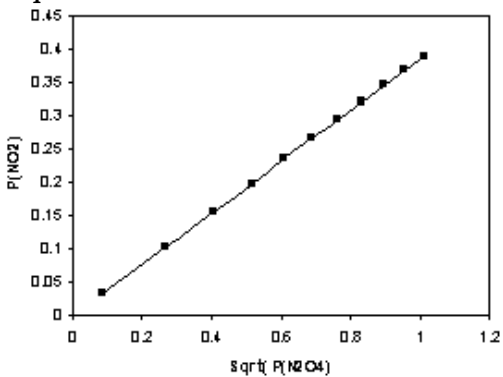
$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

To test the accuracy of this equation and to find the value of K_p , we return to [\[link\]](#) and add another column in which we calculate the value of K_p for each of the data points. [\[link\]](#) makes it clear that the "constant" in [\[link\]](#) truly is independent of both the initial conditions and the equilibrium partial pressure of either one of the reactant or product. We thus refer to the constant K_p in [\[link\]](#) as the **reaction equilibrium constant**.

Relationship of Pressure of Product to Initial Amount of Reactant



Equilibrium Partial Pressures



Initial $n_{N_2O_4}$	$P_{N_2O_4}$ (atm)	P_{NO_2} (atm)	K_p

Initial $n_{N_2O_4}$	$P_{N_2O_4}$ (atm)	P_{NO_2} (atm)	K_p
0.1	0.00764	0.0336	0.148
0.5	0.0710	0.102	0.148
1	0.166	0.156	0.148
1.5	0.267	0.198	0.148
2	0.371	0.234	0.148
2.5	0.478	0.266	0.148
3	0.586	0.294	0.148
3.5	0.695	0.320	0.148
4	0.805	0.345	0.148
4.5	0.916	0.368	0.148
5	1.027	0.389	0.148

Equilibrium Partial Pressures in Decomposition Reaction

It is very interesting to note the functional form of the equilibrium constant. The product NO_2 pressure appears in the numerator, and the exponent 2 on the pressure is the stoichiometric coefficient on NO_2 in the balanced chemical equation. The reactant N_2O_4 pressure appears in the denominator, and the exponent 1 on the pressure is the stoichiometric coefficient on N_2O_4 in the chemical equation.

We now investigate whether other reactions have equilibrium constants and whether the form of this equilibrium constant is a happy coincidence or a general observation. We return to the reaction for the [synthesis of ammonia](#).

In a [previous section](#), we considered only the equilibrium produced when 1 mole of N_2 is reacted with 3 moles of H_2 . We now consider a range of possible initial values of these amounts, with the resultant equilibrium partial pressures given in

[\[link\]](#). In addition, anticipating the possibility of an equilibrium constant, we have calculated the ratio of partial pressures given by:

Equation:

$$K_p = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}$$

In [\[link\]](#), the equilibrium partial pressures of the gases are in a very wide variety, including whether the final pressures are greater for reactants or products. However, from the data in [\[link\]](#), it is clear that, despite these variations, K_p in [\[link\]](#) is essentially a constant for all of the initial conditions examined and is thus the **reaction equilibrium constant** for [this reaction](#).

V (L)	n_{N_2}	n_{H_2}	P_{N_2}	P_{H_2}	P_{NH_3}	K_p
10	1	3	0.0342	0.1027	4.82	6.2×10^5
10	0.1	0.3	0.0107	0.0322	0.467	6.0×10^5
100	0.1	0.3	0.00323	0.00968	0.0425	6.1×10^5
100	3	3	0.492	0.00880	0.483	6.1×10^5
100	1	3	0.0107	0.0322	0.467	6.0×10^5
1000	1.5	1.5	0.0255	0.00315	0.0223	6.2×10^5

Equilibrium Partial Pressures of the Synthesis of Ammonia

Studies of many chemical reactions of gases result in the same observations. Each reaction equilibrium can be described by an equilibrium constant in which the partial pressures of the products, each raised to their corresponding stoichiometric coefficient, are multiplied together in the numerator, and the partial pressures of

the reactants, each raised to their corresponding stoichiometric coefficient, are multiplied together in the denominator. For historical reasons, this general observation is sometimes referred to as the **Law of Mass Action**.

Observation 3: Temperature Dependence of the Reaction Equilibrium

We have previously observed that phase equilibrium, and in particular vapor pressure, depend on the temperature, but we have not yet studied the variation of reaction equilibrium with temperature. We focus our initial study on [this reaction](#) and we measure the equilibrium partial pressures at a variety of temperatures. From these measurements, we can compile the data showing the temperature dependence of the equilibrium constant K_p for this reaction in [\[link\]](#).

T (K)	K_p
500	6.25×10^{-3}
550	8.81×10^{-3}
650	1.49×10^{-2}
700	1.84×10^{-2}
720	1.98×10^{-2}

Equilibrium Constant for the Synthesis of HI

Note that the equilibrium constant increases dramatically with temperature. As a result, at equilibrium, the pressure of HI must also increase dramatically as the temperature is increased.

These data do not seem to have a simple relationship between K_p and temperature. We must appeal to arguments based on Thermodynamics, from which it is possible

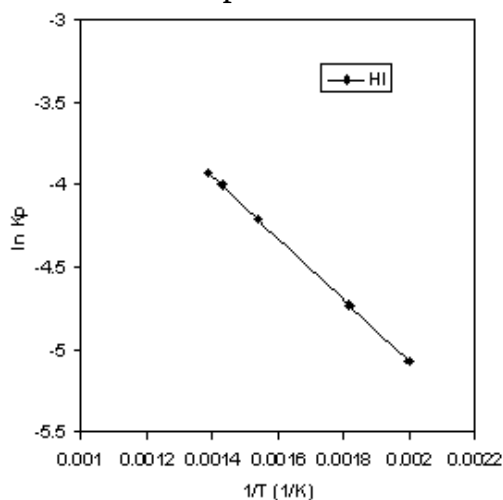
to show that the equilibrium constant should vary with temperature according to the following equation:

Equation:

$$\ln(K_p) = -\frac{\Delta(H^\circ)}{RT} + \frac{\Delta(S^\circ)}{R}$$

If $\Delta(H^\circ)$ and $\Delta(S^\circ)$ do not depend strongly on the temperature, then this equation would predict a simple straight line relationship between $\ln(K_p)$ and $\frac{1}{T}$. In addition, the slope of this line should be $-\frac{\Delta(H^\circ)}{R}$. We test this possibility with the graph in [\[link\]](#).

Inverse of Temperature vs. Natural Log of Equilibrium Constant



In fact, we do observe a straight line through the data. In this case, the line has a negative slope. Note carefully that this means that K_p is **increasing** with temperature. The negative slope via [\[link\]](#) means that $-\frac{\Delta(H^\circ)}{R}$ must be negative, and indeed for [this reaction](#) in this temperature range, $\Delta(H^\circ) = 15.6 \frac{\text{kJ}}{\text{mol}}$. This value matches well with the slope of the line in [\[link\]](#).

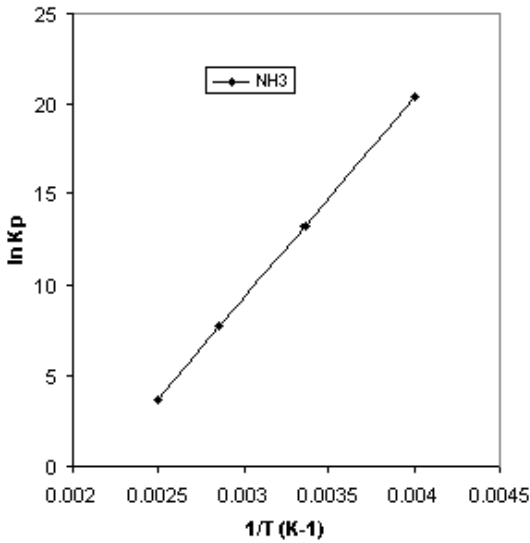
Given the validity of [\[link\]](#) in describing the temperature dependence of the equilibrium constant, we can also predict that an exothermic reaction with $\Delta(H^\circ) < 0$ should have a positive slope in the graph of $\ln(K_p)$ versus $\frac{1}{T}$, and thus the equilibrium constant should **decrease** with increasing temperature. A good example of an exothermic reaction is the [synthesis of ammonia](#) for which $\Delta(H^\circ) = -99.2 \frac{\text{kJ}}{\text{mol}}$. Equilibrium constant data are given in [\[link\]](#). Note that, as

predicted, the equilibrium constant for this exothermic reaction decreases rapidly with increasing temperature. The data from [\[link\]](#) is shown in [\[link\]](#), clearly showing the contrast between the endothermic reaction and the exothermic reaction. The slope of the graph is positive for the exothermic reaction and negative for the endothermic reaction. From [\[link\]](#), this is a general result for all reactions.

T (K)	K_p
250	7×10^8
298	6×10^5
350	2×10^3
400	36

Equilibrium Constant for the Synthesis of Ammonia

Inverse of Temperature vs. Natural Log of Equilibrium Constant



Observation 4: Changes in Equilibrium and Le Châtelier's Principle

One of our goals at the outset was to determine whether it is possible to control the equilibrium which occurs during a gas reaction. We might want to force a reaction to produce as much of the products as possible. In the alternative, if there are unwanted by-products of a reaction, we might want conditions which minimize the product. We have observed that the amount of product varies with the quantities of initial materials and with changes in the temperature. Our goal is a systematic understanding of these variations.

A look back at [\[link\]](#) and [\[link\]](#) shows that the equilibrium pressure of the product of the reaction increases with increasing the initial quantity of reaction. This seems quite intuitive. Less intuitive is the variation of the equilibrium pressure of the product of [this reaction](#) with variation in the volume of the container, as shown in [\[link\]](#). Note that the pressure of NH_3 decreases by more than a factor of ten when the volume is increased by a factor of ten. This means that, at equilibrium, there are fewer moles of NH_3 produced when the reaction occurs in a larger volume.

To understand this effect, we rewrite the equilibrium constant in [\[link\]](#) to explicit show the volume of the container. This is done by applying **Dalton's Law of Partial Pressures**, so that each partial pressure is given by the Ideal Gas Law:
Equation:

$$\begin{aligned} K_p &= \frac{n_{NH_3}^2 \left(\frac{RT}{V}\right)^2}{n_{N_2} \frac{RT}{V} n_{H_2}^3 \left(\frac{RT}{V}\right)^3} \\ &= \frac{n_{NH_3}^2}{n_{N_2} n_{H_2}^3 \left(\frac{RT}{V}\right)^2} \end{aligned}$$

Therefore,
Equation:

$$K_p \left(\frac{RT}{V}\right)^2 = \frac{n_{NH_3}^2}{n_{N_2} n_{H_2}^3}$$

This form of the equation makes it clear that, when the volume increases, the left side of the equation decreases. This means that the right side of the equation must decrease also, and in turn, n_{NH_3} must decrease while n_{N_2} and n_{H_2} must increase. The equilibrium is thus shifted from products to reactants when the volume increases for [this reaction](#).

The effect of changing the volume must be considered for each specific reaction, because the effect depends on the stoichiometry of the reaction. One way to determine the consequence of a change in volume is to rewrite the equilibrium constant as we have done in [\[link\]](#).

Finally, we consider changes in temperature. We note that K_p increases with T for endothermic reactions and decreases with T for exothermic reactions. As such, the products are increasingly favored with increasing temperature when the reaction is endothermic, and the reactants are increasingly favored with increasing temperature when the reaction is exothermic. On reflection, we note that when the reaction is exothermic, the reverse reaction is endothermic. Putting these statements together, we can say that the reaction equilibrium always shifts in the direction of the endothermic reaction when the temperature is increased.

All of these observations can be collected into a single unifying concept known as **Le Châtelier's Principle**.

Principle

Le Châtelier's Principle

When a reaction at equilibrium is stressed by a change in conditions, the equilibrium will be reestablished in such a way as to counter the stress.

This statement is best understood by reflection on the types of "stresses" we have considered in this section. When a reactant is added to a system at equilibrium, the reaction responds by consuming some of that added reactant as it establishes a new equilibrium. This offsets some of the stress of the increase in reactant. When the temperature is raised for a reaction at equilibrium, this adds thermal energy. The system shifts the equilibrium in the endothermic direction, thus absorbing some of the added thermal energy, countering the stress.

The most challenging of the three types of stress considered in this section is the change in volume. By increasing the volume containing a gas phase reaction at equilibrium, we reduce the partial pressures of all gases present and thus reduce the total pressure. Recall that the response of [this reaction](#) to the volume increase was to create more of the reactants at the expense of the products. One consequence of this shift is that more gas molecules are created, and this increases the total pressure in the reaction flask. Thus, the reaction responds to the stress of the volume increase by partially offsetting the pressure decrease with an increase in the number of moles of gas at equilibrium.

Le Châtelier's principle is a useful mnemonic for predicting how we might increase or decrease the amount of product at equilibrium by changing the conditions of the reaction. From this principle, we can predict whether the reaction should occur at high temperature or low temperature, and whether it should occur at high pressure or low pressure.

Review and Discussion Questions

Exercise:

Problem:

In the data given for equilibrium of [this reaction](#), there is no volume given. Show that changing the volume for the reaction does not change the number of moles of reactants and products present at equilibrium, i.e. changing the volume does not shift the equilibrium.

Exercise:

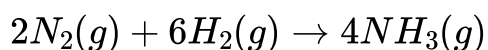
Problem:

For [this reaction](#) the number of moles of NO_2 at equilibrium increases if we increase the volume in which the reaction is contained. Explain why this must be true in terms of dynamic equilibrium, give a reason why the rates of the forward and reverse reactions might be affected differently by changes in the volume.

Exercise:

Problem: We could balance [\[link\]](#) by writing

Equation:



Write the form of the equilibrium constant for the reaction balanced as in [\[link\]](#). What is the value of the equilibrium constant? (Refer to [\[link\]](#).) Of course, the pressures at equilibrium do not depend on whether the reaction is balanced as in [\[link\]](#) or as in [\[link\]](#). Explain why this is true, even though the equilibrium constant can be written differently and have a different value.

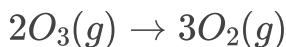
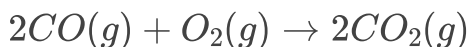
Exercise:

Problem:

Show that the equilibrium constant K_p in [\[link\]](#) for [this reaction](#) can be written in terms of the concentrations or particle densities, e.g. $[N_2] = \frac{n_{N_2}}{V}$, instead of the partial pressures. In this form, we call the equilibrium constant K_c . Find the relationship between K_p and K_c , and calculate the value of K_c .

Exercise:**Problem:**

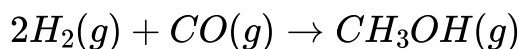
For each of these reactions, predict whether increases in temperature will shift the reaction equilibrium more towards products or more towards reactants.

**Exercise:****Problem:**

Plot the data in [\[link\]](#) on a graph showing K_p on the y-axis and T on the x-axis. The shape of this graph is reminiscent of the graph of another physical property as a function of increasing temperature. Identify that property, and suggest a reason why the shapes of the graphs might be similar.

Exercise:**Problem:**

Using Le Châtelier's principle, predict whether the specified "stress" will produce an increase or a decrease in the amount of product observed at equilibrium for the reaction:

Equation:

$$\Delta(H^\circ) = -91 \frac{\text{kJ}}{\text{mol}}$$

Volume of container is increased.

Helium is added to container.

Temperature of container is raised.

Hydrogen is added to container.

CH_3OH is extracted from container as it is formed.

Acid-Base Equilibrium

Foundation

We have developed an understanding of **equilibrium** involving phase transitions and involving reactions entirely in the gas phase. We will assume an understanding of the principles of dynamic equilibrium, reaction equilibrium constants, and **Le Châtelier's Principle**. To understand application of these principles to reactions in solution, we will now assume a definition of certain classes of substances as being either acids or bases. An acid is a substance whose molecules donate positive hydrogen ions (protons) to other molecules or ions. When dissolved in pure water, acid molecules will transfer a hydrogen ion to a water molecule or to a cluster of several water molecules. This increases the concentration of H^+ ions in the solution. A base is a substance whose molecules accept hydrogen ions from other molecules. When dissolved in pure water, base molecules will accept a hydrogen ion from a water molecule, leaving behind an increased concentration of OH^- ions in the solution. To understand what determines acid-base behavior, we will assume an understanding of the bonding, structure, and properties of individual molecules.

Goals

Acids and bases are very common substances whose properties vary greatly. Many acids are known to be quite corrosive, with the ability to dissolve solid metals or burn flesh. Many other acids, however, are not only benign but vital to the processes of life. Far from destroying biological molecules, they carry out reactions critical for organisms. Similarly, many bases are caustic cleansers while many others are medications to calm indigestion pains.

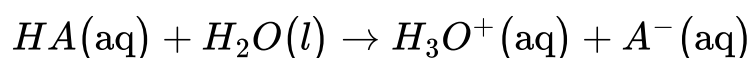
In this concept study, we will develop an understanding of the characteristics of molecules which make them either acids or bases. We will examine measurements about the relative strengths of acids and bases, and we will use these to develop a quantitative understanding of the relative strengths of acids and bases. From this, we can develop a qualitative understanding of the properties of molecules which determine whether a molecule is a strong acid or a weak acid, a strong base or a weak base. This understanding is valuable in predicting the outcomes of reactions, based on the relative quantitative strengths of acids and bases. These reactions are commonly referred to as neutralization

reactions. A surprisingly large number of reactions, particularly in organic chemistry, can be understood as transfer of hydrogen ions from acid molecules to base molecules.

Observation 1: Strong Acids and Weak Acids

From the definition of an acid given in the Foundation, a typical acid can be written as HA , representing the hydrogen ion which will be donated and the rest of the molecule which will remain as a negative ion after the donation. The typical reaction of an acid in aqueous solution reacting with water can be written as

Equation:



In this reaction, $HA(aq)$ represents an acid molecule dissolved in aqueous solution. $H_3O^+(aq)$ is a notation to indicate that the donated proton has been dissolved in solution. Observations indicate that the proton is associated with several water molecules in a cluster, rather than attached to a single molecule. H_3O^+ is a simplified notation to represent this result. Similarly, the $A^-(aq)$ ion is solvated by several water molecules. [\[link\]](#) is referred to as **acid ionization**.

[\[link\]](#) implies that a 0.1M solution of the acid HA in water should produce H_3O^+ ions in solution with a concentration of 0.1M. In fact, the concentration of H_3O^+ ions, $[H_3O^+]$, can be measured by a variety of techniques. Chemists commonly use a measure of the H_3O^+ ion concentration called the pH, defined by:

$$\text{pH} = -\log [H_3O^+]$$

We now observe the concentration $[H_3O^+]$ produced by dissolving a variety of acids in solution at a concentration of 0.1M, and the results are tabulated in [\[link\]](#).

Acid	$[H_3O^+]$ (M)	pH
H_2SO_4	0.1	1
HNO_3	0.1	1
HCl	0.1	1
HBr	0.1	1
HI	0.1	1
$HClO_4$	0.1	1
$HClO_3$	0.1	1
HNO_2	6.2×10^{-3}	2.2
HCN	7×10^{-6}	5.1
HIO	1×10^{-6}	5.8
HF	5.5×10^{-3}	2.3
$HOCN$	5.5×10^{-3}	2.3
$HClO_2$	2.8×10^{-2}	1.6
CH_3COOH (acetic acid)	1.3×10^{-3}	2.9
CH_3CH_2COOH (propionic acid)	1.1×10^{-3}	2.9

H_3O^+ pH for 0.1M Acid Solutions

Note that there are several acids listed for which $[H_3O^+] = 0.1M$, and $pH = 1$. This shows that, for these acids, the acid ionization is complete: essentially every acid molecule is ionized in the solution according to [\[link\]](#). However, there are other acids listed for which $[H_3O^+]$ is considerably less

than 0.1M and the pH is considerably greater than 1. For each of these acids, therefore, not all of the acid molecules ionize according to [\[link\]](#). In fact, it is clear in [\[link\]](#) that in these acids the vast majority of the acid molecules do not ionize, and only a small percentage does ionize.

From these observations, we distinguish two classes of acids: **strong acids** and **weak acids**. Strong acids are those for which nearly 100% of the acid molecules ionize, whereas weak acids are those for which only a small percentage of molecules ionize. There are seven strong acids listed in [\[link\]](#). From many observations, it is possible to determine that these seven acids are the only commonly observed strong acids. The vast majority of all substances with acidic properties are weak acids. We seek to characterize weak acid ionization quantitatively and to determine what the differences in molecular properties are between strong acids and weak acids.

Observation 2: Percent Ionization in Weak Acids

[\[link\]](#) shows that the pH of 0.1M acid solutions varies from one weak acid to another. If we dissolve 0.1 moles of acid in a 1.0L solution, the fraction of those acid molecules which will ionize varies from weak acid to weak acid. For a few weak acids, using the data in [\[link\]](#) we calculate the percentage of ionized acid molecules in 0.1M acid solutions in [\[link\]](#).

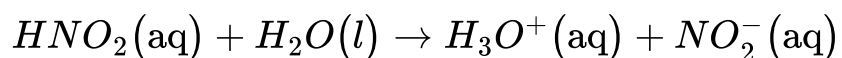
Acid	$[H_3O^+]$ (M)	% ionization
HNO_2	6.2×10^{-3}	6.2%
HCN	7×10^{-6}	0.007%
HIO	1×10^{-6}	0.001%
HF	5.5×10^{-3}	5.5%

Acid	$[H_3O^+]$ (M)	% ionization
$HOCN$	5.5×10^{-3}	5.5%
$HClO_2$	2.8×10^{-2}	28.2%
CH_3COOH (acetic acid)	1.3×10^{-3}	1.3%
CH_3CH_2COOH (propionic acid)	1.1×10^{-3}	1.1%

Percent Ionization of 0.1M Acid Solutions

We might be tempted to conclude from [\[link\]](#) that we can characterize the strength of each acid by the percent ionization of acid molecules in solution. However, before doing so, we observe the pH of a single acid, nitrous acid, in solution as a function of the concentration of the acid.

Equation:



In this case, "concentration of the acid" refers to the number of moles of acid that we dissolved per liter of water. Our observations are listed in [\[link\]](#), which gives $[H_3O^+]$, pH, and percent ionization as a function of nitrous acid concentration.

c_0 (M)	$[H_3O^+]$	pH	% Ionization
0.50	1.7×10^{-2}	1.8	3.3%
0.20	1.0×10^{-2}	2.0	5.1%
0.10	7.0×10^{-3}	2.2	7.0%

c_0 (M)	$[H_3O^+]$	pH	% Ionization
0.050	4.8×10^{-3}	2.3	9.7%
0.020	2.9×10^{-3}	2.5	14.7%
0.010	2.0×10^{-3}	2.7	20.0%
0.005	1.3×10^{-3}	2.9	26.7%
0.001	4.9×10^{-4}	3.3	49.1%
0.0005	3.0×10^{-4}	3.5	60.8%

% Ionization of Nitrous Acid

Surprisingly, perhaps, the percent ionization varies considerably as a function of the concentration of the nitrous acid. We recall that this means that the fraction of molecules which ionize, according to [\[link\]](#), depends on how many acid molecules there are per liter of solution. Since some but not all of the acid molecules are ionized, this means that nitrous acid molecules are present in solution at the same time as the negative nitrite ions and the positive hydrogen ions. Recalling our observation of equilibrium in gas phase reactions, we can conclude that [\[link\]](#) achieves equilibrium for each concentration of the nitrous acid.

Since we know that gas phase reactions come to equilibrium under conditions determined by the equilibrium constant, we might speculate that the same is true of reactions in aqueous solution, including acid ionization. We therefore define an analogy to the gas phase reaction equilibrium constant. In this case, we would not be interested in the pressures of the components, since the reactants and products are all in solution. Instead, we try a function composed of the equilibrium concentrations:

Equation:

$$K = \frac{[H_3O^+][NO_2^-]}{[HNO_2][H_2O]}$$

The concentrations at equilibrium can be calculated from the data in [\[link\]](#) for nitrous acid. $[H_3O^+]$ is listed and $[NO_2^-] = [H_3O^+]$. Furthermore, if c_0 is the initial concentration of the acid defined by the number of moles of acid dissolved in solution per liter of solution, then $[HA] = c_0 - [H_3O^+]$. Note that the contribution of $[H_2O(l)]$ to the value of the function K is simply a constant. This is because the "concentration" of water in the solution is simply the molar density of water, $\frac{n_{H_2O}}{V} = 55.5M$, which is not affected by the presence or absence of solute. All of the relevant concentrations, along with the function in [\[link\]](#) are calculated and tabulated in [\[link\]](#).

c_0 (M)	$[H_3O^+]$	$[NO_2^-]$	$[HNO_2]$	K
0.50	1.7×10^{-2}	1.7×10^{-2}	0.48	1.0×10^{-5}
0.20	1.0×10^{-2}	1.0×10^{-2}	0.19	9.9×10^{-6}
0.10	7.0×10^{-3}	7.0×10^{-3}	9.3×10^{-2}	9.6×10^{-6}
0.050	4.8×10^{-3}	4.8×10^{-3}	4.5×10^{-2}	9.4×10^{-6}
0.020	2.9×10^{-3}	2.9×10^{-3}	4.5×10^{-2}	9.4×10^{-6}
0.010	2.0×10^{-3}	2.0×10^{-3}	8.0×10^{-3}	8.9×10^{-6}
0.005	1.3×10^{-3}	1.3×10^{-3}	3.6×10^{-3}	8.8×10^{-6}
0.001	4.9×10^{-4}	4.9×10^{-4}	5.1×10^{-4}	8.5×10^{-6}
0.0005	3.0×10^{-4}	3.0×10^{-4}	2.0×10^{-4}	8.5×10^{-6}

Equilibrium Concentrations and K for Nitrous Acid

We note that the function K in [\[link\]](#) is approximately, though only approximately, the same for all conditions analyzed in [\[link\]](#). Variation of the concentration by a factor of 1000 produces a change in K of only 10% to 15%. Hence, we can regard the function K as a constant which approximately describes the acid ionization equilibrium for nitrous acid. By convention, chemists omit the constant concentration of water from the equilibrium expression, resulting in the **acid ionization equilibrium constant**, K_a , defined as:

Equation:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

From an average of the data in [\[link\]](#), we can calculate that, at 25°C for nitrous acid, $K_a = 5 \times 10^{-4}$. Acid ionization constants for the other weak acids in [\[link\]](#) are listed in [\[link\]](#).

Acid	K_a	pK_a
HNO_2	5×10^{-4}	3.3
HCN	4.9×10^{-10}	9.3
HIO	2.3×10^{-11}	10.6
HF	3.5×10^{-4}	3.4
$HOCN$	3.5×10^{-4}	3.4
$HClO_2$	1.1×10^{-2}	2.0
CH_3COOH (acetic acid)	1.7×10^{-5}	4.8

Acid	K_a	pK_a
CH_3CH_2COOH (propionic acid)	1.4×10^{-5}	4.9

Weak Acid Ionization Constants, K_a and pK_a

We make two final notes about the results in [\[link\]](#). First, it is clear the larger the value of K_a , the stronger the acid. That is, when K_a is a larger number, the percent ionization of the acid is larger, and vice versa. Second, the values of K_a vary over many orders of magnitude. As such, it is often convenient to define the quantity pK_a , analogous to pH, for purposes of comparing acid strengths:

Equation:

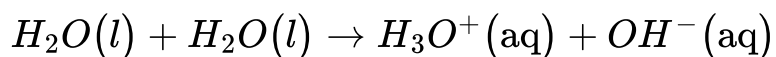
$$pK_a = -\log K_a$$

The value of pK_a for each acid is also listed in [\[link\]](#). Note that a small value of pK_a implies a large value of K_a and thus a stronger acid. Weaker acids have larger values of pK_a . K_a and pK_a thus give a simple quantitative comparison of the strength of weak acids.

Observation 3: Autoionization of Water

Since we have the ability to measure pH for acid solutions, we can measure pH for pure water as well. It might seem that this would make no sense, as we would expect $[H_3O^+]$ to equal zero exactly in pure water. Surprisingly, this is incorrect: a measurement on pure water at 25°C yields $pH = 7$, so that $[H_3O^+] = 1.0 \times 10^{-7} M$. There can be only one possible source for these ions: water molecules. The process

Equation:



is referred to as the **autoionization** of water. Note that, in this reaction, some water molecules behave as acid, donating protons, while other water molecules behave as base, accepting protons.

Since at equilibrium $[H_3O^+] = 1.0 \times 10^{-7} M$, it must also be true that $[OH^-] = 1.0 \times 10^{-7} M$. We can write the equilibrium constant for [\[link\]](#), following our previous convention of omitting the pure water from the expression, and we find that, at 25°C,

Equation:

$$\begin{aligned} K_w &= [H_3O^+] [OH^-] \\ &= 1.0 \times 10^{-14} M \end{aligned}$$

(In this case, the subscript "w" refers to "water".)

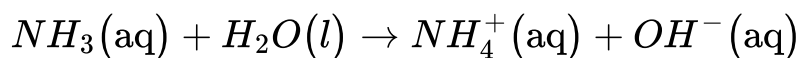
[\[link\]](#) occurs in pure water but must also occur when ions are dissolved in aqueous solutions. This includes the presence of acids ionized in solution. For example, we consider a solution of 0.1M acetic acid. Measurements show that, in this solution $[H_3O^+] = 1.3 \times 10^{-3} M$ and $[OH^-] = 7.7 \times 10^{-12} M$. We note two things from this observation: first, the value of $[OH^-]$ is considerably less than in pure water; second, the autoionization equilibrium constant remains the same at 1.0×10^{-14} . From these notes, we can conclude that the autoionization equilibrium of water occurs in acid solution, but the extent of autoionization is suppressed by the presence of the acid in solution.

We consider a final note on the autoionization of water. The pH of pure water is 7 at 25°C. Adding any acid to pure water, no matter how weak the acid, must increase $[H_3O^+]$, thus producing a pH below 7. As such, we can conclude that, for all acid solutions, pH is less than 7, or on the other hand, any solution with pH less than 7 is acidic.

Observation 4: Base Ionization, Neutralization and Hydrolysis of Salts

We have not yet examined the behavior of base molecules in solution, nor have we compared the relative strengths of bases. We have defined a base molecule as one which accepts a positive hydrogen ion from another molecule. One of the most common examples is ammonia, NH_3 . When ammonia is dissolved in aqueous solution, the following reaction occurs:

Equation:



Due to the lone pair of electrons on the highly electronegative N atom, NH_3 molecules will readily attach a free hydrogen ion forming the ammonium ion NH_4^+ . When we measure the concentration of OH^- for various initial concentration of NH_3 in water, we observe the results in [\[link\]](#). We should anticipate that a base ionization equilibrium constant might exist comparable to the acid ionization equilibrium constant, and in [\[link\]](#), we have also calculated the value of the function K_b defined as:

Equation:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

c_0 (M)	$[OH^-]$	K_b	pH
0.50	3.2×10^{-3}	2.0×10^{-5}	11.5
0.20	2.0×10^{-3}	2.0×10^{-5}	11.3
0.10	1.4×10^{-3}	2.0×10^{-5}	11.1
0.050	9.7×10^{-4}	1.9×10^{-5}	11.0
0.020	6.0×10^{-4}	1.9×10^{-5}	10.8
0.010	4.2×10^{-4}	1.9×10^{-5}	10.6
0.005	3.0×10^{-4}	1.9×10^{-5}	10.5
0.001	1.3×10^{-4}	1.8×10^{-5}	10.1

c_0 (M)	$[OH^-]$	K_b	pH
0.0005	8.7×10^{-5}	1.8×10^{-5}	9.9

Equilibrium Concentrations and K_b for Ammonia

Given that we have dissolved a base in pure water, we might be surprised to discover the presence of positive hydrogen ions, H_3O^+ , in solution, but a measurement of the pH for each of the solutions reveals small amounts. The pH for each solution is also listed in [\[link\]](#). The source of these H_3O^+ ions must be the autoionization of water. Note, however, that in each case in basic solution, the concentration of H_3O^+ ions is less than that in pure water. Hence, the presence of the base in solution has suppressed the autoionization. Because of this, in each case the pH of a basic solution is greater than 7.

Base ionization is therefore quite analogous to acid ionization observed earlier. We now consider a comparison of the strength of an acid to the strength of a base. To do so, we consider a class of reactions called "neutralization reactions" which occur when we mix an acid solution with a base solution. Since the acid donates protons and the base accepts protons, we might expect, when mixing acid and base, to achieve a solution which is no longer acidic or basic. For example, if we mix together equal volumes of 0.1M $HCl(aq)$ and 0.1M $NaOH(aq)$, the following reaction occurs:

Equation:



The resultant solution is simply a salt solution with $NaCl$ dissolved in water. This solution has neither acidic nor basic properties, and the pH is 7; hence the acid and base have neutralized each other. In this case, we have mixed together a strong acid with a strong base. Since both are strong and since we mixed equal molar quantities of each, the neutralization reaction is essentially complete.

We next consider mixing together a weak acid solution with a strong base solution, again with equal molar quantities of acid and base. As an example, we mix 100ml of 0.1M acetic acid (HA) solution with 100ml of 0.1M sodium hydroxide. In this discussion, we will abbreviate the acetic acid molecular

formula CH_3COOH as HA and the acetate ion CH_3COO^- as A^- . The reaction of HA and $NaOH$ is:

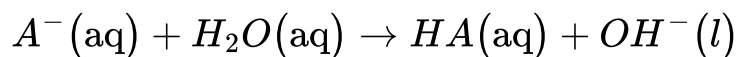
Equation:



$A^-(aq)$ is the acetate ion in solution, formed when an acetic acid molecule donates the positive hydrogen ion. We have thus created a salt solution again, in this case of sodium acetate in water. Note that the volume of the combined solution is 200ml, so the concentration of sodium acetate (NaA) in solution is 0.050M.

Unlike our previous $NaCl$ salt solution, a measurement in this case reveals that the pH of the product salt solution is 9.4, so the solution is basic. Thus, mixing equal molar quantities of strong base with weak acid produces a basic solution. In essence, the weak acid does not fully neutralize the strong base. To understand this, we examine the behavior of sodium acetate in solution. Since the pH is greater than 7, then there is an excess of OH^- ions in solution relative to pure water. These ions must have come from the reaction of sodium acetate with the water. Therefore, the negative acetate ions in solution must behave as a base, accepting positive hydrogen ions:

Equation:



The reaction of an ion with water to form either an acid or a base solution is referred to as **hydrolysis**. From this example, the salt of a weak acid behaves as a base in water, resulting in a pH greater than 7.

To understand the extent to which the hydrolysis of the negative ion occurs, we need to know the equilibrium constant for this reaction. This turns out to be determined by the acid ionization constant for HA . To see this, we write the equilibrium constant for the hydrolysis of A^- as

Equation:

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

Multiplying numerator and denominator by $[H_3O^+]$, we find that

Equation:

$$\begin{aligned}K_h &= \frac{[HA][OH^-]}{[A^-]} \frac{[H_3O^+]}{[H_3O^+]} \\&= \frac{K_w}{K_a}\end{aligned}$$

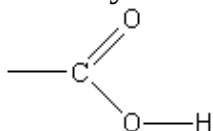
Therefore, for the hydrolysis of acetate ions in solution, $K_h = 5.8 \times 10^{-10}$. This is fairly small, so the acetate ion is a very weak base.

Observation 5: Acid strength and molecular properties

We now have a fairly complete quantitative description of acid-base equilibrium. To complete our understanding of acid-base equilibrium, we need a predictive model which relates acid strength or base strength to molecular properties. In general, we expect that the strength of an acid is related either to the relative ease by which it can donate a hydrogen ion or by the relative stability of the remaining negative ion formed after the departure of the hydrogen ion.

To begin, we note that there are three basic categories of acids which we have examined in this study. First, there are simple **binary acids**: HF HCl HBr HI . Second, there are acids formed from main group elements combined with one or more oxygen atoms, such H_2SO_4 or HNO_3 . These are called **oxyacids**. Third, there are the **carboxylic acids**, organic molecules which contain the carboxylic functional group in [\[link\]](#).

Carboxylic Functional Group



We consider first the simple binary acids. HCl , HBr , and HI are all strong acids, whereas HF is a weak acid. In comparing the experimental values of pK_a values in [\[link\]](#), we note that the acid strength increases in the order $HF < HCl < HBr < HI$. This means that the hydrogen ion can more readily separate from the covalent bond with the halogen atom (X) as we move down the periodic table. This is reasonable, because the strength of the H-X bond also decreases as we move down the periodic table, as shown in [\[link\]](#).

	pK_a	Bond Energy ($\frac{\text{kJ}}{\text{mol}}$)
HF	3.1	567.7
HCl	-6.0	431.6
HBr	-9.0	365.9
HI	-9.5	298.0

H-X Bond Strengths and pK_a

The decreasing strength of the H-X bond is primarily due to the increase in the size of the X atom as we move down the periodic table. We conclude that one factor which influences acidity is the strength of the H-X bond: a weaker bond produces a stronger acid, and vice versa.

In the acids in the other two categories, the hydrogen atom which ionizes is attached directly to an oxygen atom. Thus, to understand acidity in these molecules, we must examine what the oxygen atom is in turn bonded to. It is very interesting to note that, in examining compounds like R-O-H, where R is an atom or group of atoms, we can get either acidic or basic properties. For examples, NaOH is a strong base, whereas HOCl is a weak acid. This means that, when NaOH ionizes in solution, the Na-O linkage ionizes, whereas when HOCl ionizes in solution, the H-O bond ionizes.

To understand this behavior, we compare the strength of the simple oxyacids HOI, HOBr, and HOCl. The pK_a 's for these acids are found experimentally to be, respectively, 10.6, 8.6, and 7.5. The acid strength for HOX increases as we move up the periodic table in the halogen group. This means that the H-O bond ionizes more readily when the oxygen atom is bonded to a more electronegative atom.

We can add to this observation by comparing the strengths of the acids HOCl, HOClO, HOClO₂, and HOClO₃. (Note that the molecular formulae are more commonly written as HClO, HClO₂, HClO₃, and HClO₄. We have written them instead to emphasize the molecular structure.) The pK_a 's of these acids are, respectively, 7.5, 2.0, -2.7, and -8.0. In each case, the molecule with more oxygen atoms on the central Cl atom is the stronger acid: HOClO is

more acidic than $HOCl$, etc. A similar result is found in comparing the oxyacids of nitrogen. $HONO_2$, nitric acid, is one of the strong acids, whereas $HONO$, nitrous acid, is a weak acid. Since oxygen atoms are very strongly electronegative, these trends add to our observation that increasing electronegativity of the attached atoms increases the ionization of the O-H bond.

Why would electronegativity play a role in acid strength? There are two conclusions we might draw. First, a greater electronegativity of the atom or atoms attached to the H-O in the oxyacid apparently results in a weaker H-O bond, which is thus more readily ionized. We know that an electronegative atom polarizes bonds by drawing the electrons in the molecule towards it. In this case, the Cl in $HOCl$ and the Br in $HOBr$ must polarize the H-O bond, weakening it and facilitating the ionization of the hydrogen. In comparing $HOCl$ to $HOClO$, the added oxygen atom must increase the polarization of the H-O bond, thus weakening the bond further and increasing the extent of ionization.

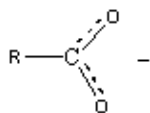
A second conclusion has to do with the ion created by the acid ionization. The negative ion produced has a surplus electron, and the relative energy of this ion will depend on how readily that extra electron is attracted to the atoms of ion. The more electronegative those atoms are, the stronger is the attraction. Therefore, the OCl^- ion can more readily accommodate the negative charge than can the OBr^- ion. And the $OClO^-$ ion can more readily accommodate the negative charge than can the OCl^- ion.

We conclude that the presence of strongly electronegative atoms in an acid increases the polarization of the H-O bond, thus facilitating ionization of the acid, and increases the attraction of the extra electron to the negative ion, thus stabilizing the negative ion. Both of these factors increase the acid strength. Chemists commonly use both of these conclusions in understanding and predicting relative acid strength.

The relative acidity of carbon compounds is a major subject of organic chemistry, which we can only visit briefly here. In each of the carboxylic acids, the H-O group is attached to a carbonyl $C=O$ group, which is in turn bonded to other atoms. The comparison we observe here is between carboxylic acid molecules, denoted as $RCOOH$, and other organic molecules containing the H-O group, such as alcohols denoted as ROH . (R is simply an atom or group

of atoms attached to the functional group.) The former are obviously acids whereas the latter group contains molecules which are generally extremely weak acids. One interesting comparison is for the acid and alcohol when R is the benzene ring, C_6H_5 . Benzoic acid, C_6H_5COOH , has $pK_a = 4.2$, whereas phenol, C_6H_5OH , has $pK_a = 9.9$. Thus, the presence of the doubly bonded oxygen atom on the carbon atom adjacent to the O-H clearly increases the acidity of the molecule, and thus increases ionization of the O-H bond.

This observation is quite reasonable in the context of our previous conclusion. Adding an electronegative oxygen atom in near proximity to the O-H bond both increases the polarization of the O-H bond and stabilizes the negative ion produced by the acid ionization. In addition to the electronegativity effect, carboxylate anions, $RCOO^-$, exhibit resonance stabilization, as seen in [\[link\]](#).



The resonance results in a sharing of the negative charge over several atoms, thus stabilizing the negative ion. This is a major contributing factor in the acidity of carboxylic acids versus alcohols.

Review and Discussion Questions

Exercise:

Problem:

Strong acids have a higher percent ionization than do weak acids. Why don't we use percent ionization as a measure of acid strength, rather than K_a ?

Exercise:

Problem:

Using the data in [\[link\]](#) for nitrous acid, plot $[H_3O^+]$ versus c_0 , the initial concentration of the acid, and versus $[HNO_2]$ the equilibrium concentration of the acid. On a second graph, plot $[H_3O^+]^2$ versus c_0 , the initial concentration of the acid, and versus $[HNO_2]$ the equilibrium concentration of the acid. Which of these results gives a straight line? Using the equilibrium constant expression, explain your answer.

Exercise:**Problem:**

Using Le Châtelier's principle, explain why the concentration of $[OH^-]$ is much lower in acidic solution than it is in neutral solution.

Exercise:**Problem:**

We considered mixing a strong base with a weak acid, but we did not consider mixing a strong acid with a weak acid. Consider mixing 0.1M HNO_3 and 0.1M HNO_2 . Predict the pH of the solution and the percent ionization of the nitrous acid. Rationalize your prediction using Le Châtelier's principle.

Exercise:**Problem:**

Imagine taking a 0.5M solution of nitrous acid and slowly adding water to it. Looking at [\[link\]](#), we see that, as the concentration of nitrous acid decreases, the percent ionization increases. By contrast, $[H_3O^+]$ decreases. Rationalize these results using Le Châtelier's principle.

Exercise:

Problem:

We observed that mixing a strong acid and a strong base, in equal amounts and concentrations, produces a neutral solution, and that mixing a strong base with a weak acid, in equal amounts and concentrations, produces a basic solution. Imagine mixing a weak acid and a weak base, in equal amounts and concentrations. Predict whether the resulting solution will be acidic, basic, or neutral, and explain your prediction.

Exercise:**Problem:**

Using the electronegativity arguments presented [above](#), explain why, in general, compounds like M-O-H are bases rather than acids, when M is a metal atom. Predict the relationship between the properties of the metal atom M and the strength of the base MOH .

Exercise:**Problem:**

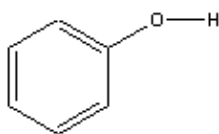
Ionization of sulfuric acid H_2SO_4 produces HSO_4^- , which is also an acid. However, HSO_4^- is a much weaker acid than H_2SO_4 . Using the conclusions from [above](#), explain why HSO_4^- is a much weaker acid.

Exercise:**Problem:**

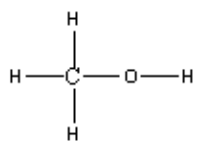
Predict and explain the relative acid strengths of H_2S and HCl . Predict and explain the relative acid strengths of H_3PO_4 and H_3AsO_4 .

Exercise:**Problem:**

Using arguments from [above](#), predict and explain the relative acidity of [phenol](#) and [methanol](#).



Phenol



Methanol

Reaction Rates

Foundation

We will assume an understanding of the postulates of the **Kinetic Molecular Theory** and of the energetics of chemical reactions. We will also assume an understanding of phase equilibrium and reaction equilibrium, including the temperature dependence of equilibrium constants.

Goals

We have carefully examined the observation that chemical reactions come to equilibrium. Depending on the reaction, the equilibrium conditions can be such that there is a mixture of reactants and products, or virtually all products, or virtually all reactants. We have not considered the time scale for the reaction to achieve these conditions, however. In many cases, the speed of the reaction might be of more interest than the final equilibrium conditions of the reaction. Some reactions proceed so slowly towards equilibrium as to appear not to occur at all. For example, metallic iron will eventually oxidize in the presence of aqueous salt solutions, but the time is sufficiently long for this process that we can reasonably expect to build a boat out of iron. On the other hand, some reactions may be so rapid as to pose a hazard. For example, hydrogen gas will react with oxygen gas so rapidly as to cause an explosion. In addition, the time scale for a reaction can depend very strongly on the amounts of reactants and their temperature.

In this concept development study, we seek an understanding of the rates of chemical reactions. We will define and measure reaction rates and develop a quantitative analysis of the dependence of the reaction rates on the conditions of the reaction, including concentration of reactants and temperature. This quantitative analysis will provide us insight into the process of a chemical reaction and thus lead us to develop a model to provide an understanding of the significance of reactant concentration and temperature.

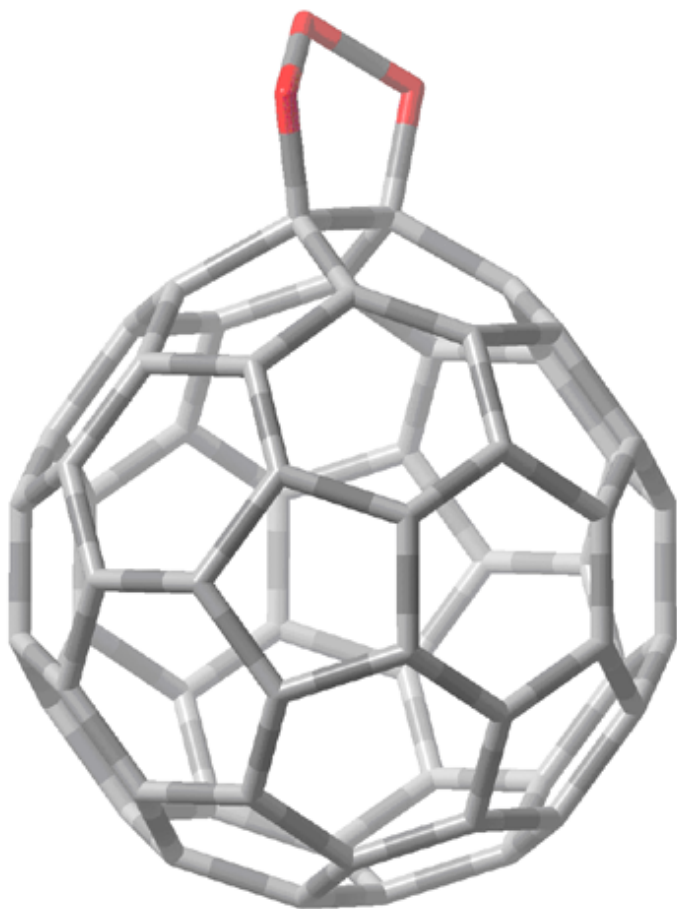
We will find that many reactions proceed quite simply, with reactant molecules colliding and exchanging atoms. In other cases, we will find that the process of reaction can be quite complicated, involving many molecular

collisions and rearrangements leading from reactant molecules to product molecules. The rate of the chemical reaction is determined by these steps.

Observation 1: Reaction Rates

We begin by considering a fairly simple reaction on a rather elegant molecule. One oxidized form of buckminsterfullerene C_{60} is $C_{60}O_3$, with a three oxygen bridge as shown in [\[link\]](#).

Oxidized Buckminsterfullerene



$C_{60}O_3$ is prepared from C_{60} dissolved in toluene solution at temperatures of $0^\circ C$ or below. When the solution is warmed, $C_{60}O_3$ decomposes, releasing O_2 and creating $C_{60}O$ in a reaction which goes essentially to completion. We can actually watch this process happen in time by measuring the amount of light of a specific frequency absorbed by the $C_{60}O_3$ molecules, called the **absorbance**. The absorbance is proportional to the concentration of the $C_{60}O_3$ in the toluene solution, so observing the absorbance as a function of

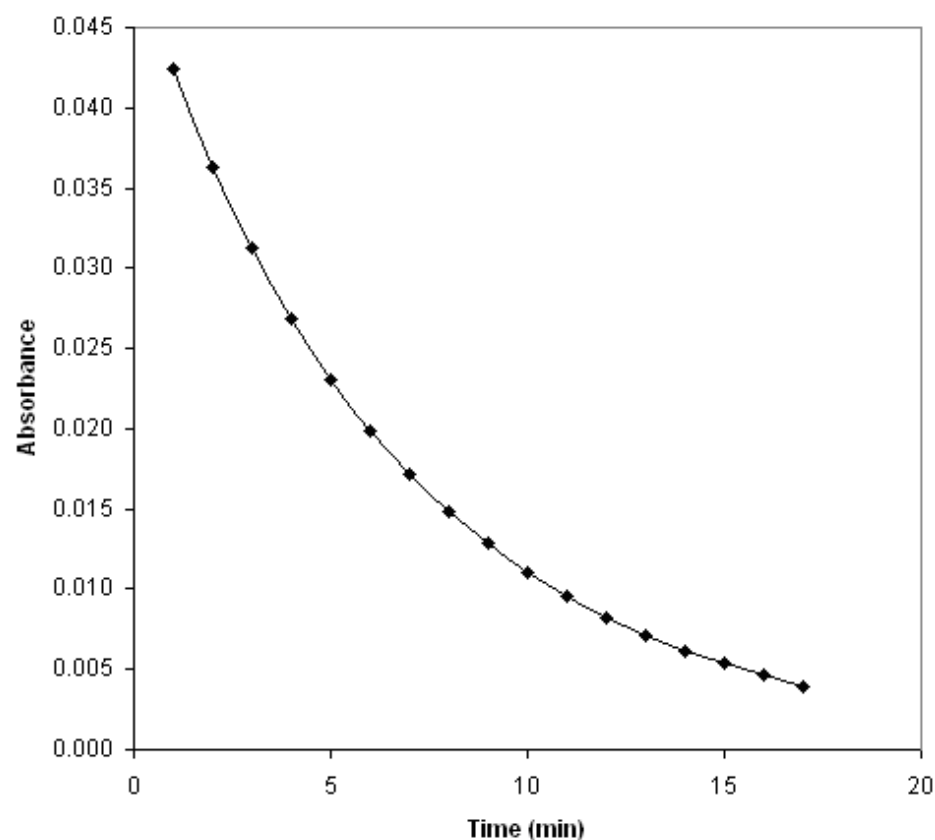
time is essentially the same as observing the concentration as a function of time. One such set of data is given in [\[link\]](#), and is shown in the graph in [\[link\]](#).

time (minutes)	$C_{60}O_3$ absorbance
3	0.04241
9	0.03634
15	0.03121
21	0.02680
27	0.02311
33	0.01992
39	0.01721
45	0.01484
51	0.01286
57	0.01106
63	0.00955
69	0.00827
75	0.00710

time (minutes)	$C_{60}O_3$ absorbance
81	0.00616
87	0.00534
93	0.00461
99	0.00395

Oxidized Buckminsterfullerene Absorbance during Thermal Decomposition at 23°C

Oxidized Buckminsterfullerene Absorbance



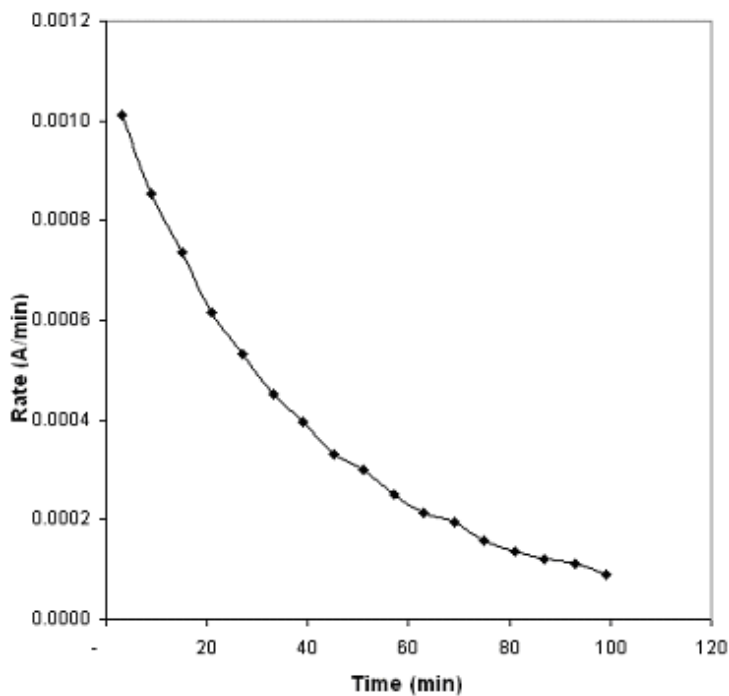
The rate at which the decomposition reaction is occurring is clearly related to the rate of change of the concentration $[C_{60}O_3]$, which is proportional to the slope of the graph in [\[link\]](#). Therefore, we define the rate of this reaction as

Equation:

$$\text{Rate} = -\frac{d [C_{60}O_3]}{d t} \simeq -\frac{\Delta([C_{60}O_3])}{\Delta(t)}$$

We want the rate of reaction to be positive, since the reaction is proceeding forward. However, because we are measuring the rate of disappearance of the reactant in this case, that rate is negative. We include a negative sign in this definition of rate so that the rate in [\[link\]](#) is a positive number. Note also that the slope of the graph in [\[link\]](#) should be taken as the derivative of the graph, since the graph is not a straight line. We will approximate that derivative by estimating the slope at each time in the data, taking the change in the absorbance of the $C_{60}O_3$ divided by the change in time at each time step. The rate, calculated in this way, is plotted as a function of time in [\[link\]](#).

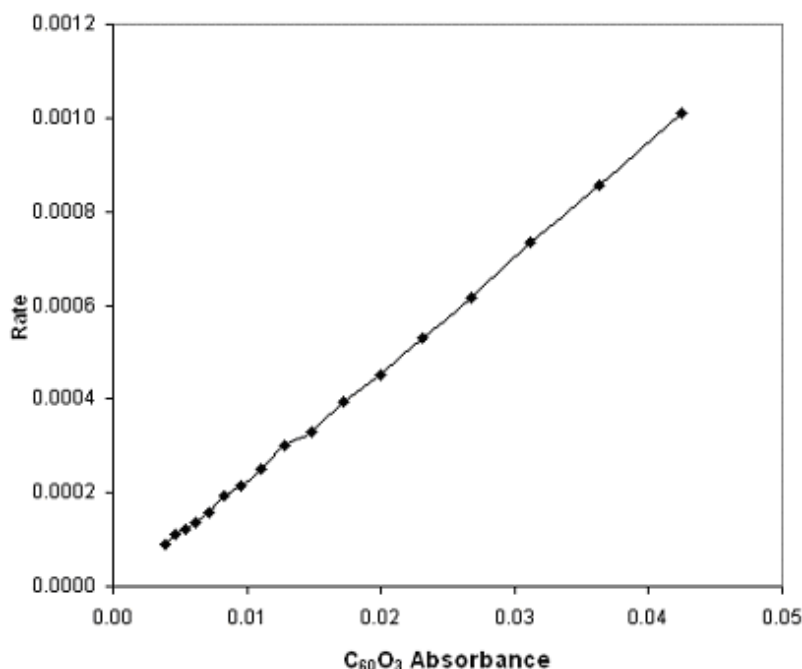
Rate of Decomposition



It is clear that the slope of the graph in [\[link\]](#) changes over the course of time. Correspondingly, [\[link\]](#) shows that the rate of the reaction decreases as the reaction proceeds. The reaction is at first very fast but then slows considerably as the reactant $C_{60}O_3$ is depleted.

The shape of the graph for rate versus time ([\[link\]](#)) is very similar to the shape of the graph for concentration versus time ([\[link\]](#)). This suggests that the rate of the reaction is related to the concentration of $C_{60}O_3$ at each time. Therefore, in [\[link\]](#), we plot the rate of the reaction, defined in [\[link\]](#) and shown in [\[link\]](#), versus the absorbance of the $C_{60}O_3$.

Rate versus Concentration



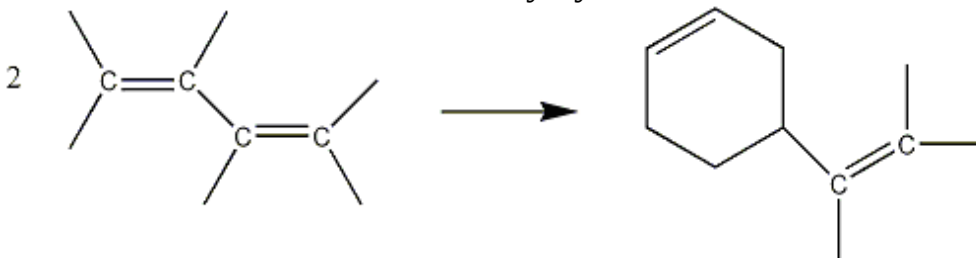
We find that there is a very simple proportional relationship between the rate of the reaction and the concentration of the reactant. Therefore, we can write **Equation:**

$$\begin{aligned}\text{Rate} &= -\frac{d[C_{60}O_3]}{dt} \\ &= k[C_{60}O_3]\end{aligned}$$

where k is a proportionality constant. This equation shows that, early in the reaction when $[C_{60}O_3]$ is large, the reaction proceeds rapidly, and that as $C_{60}O_3$ is consumed, the reaction slows down. [\[link\]](#) is an example of a **rate law**, expressing the relationship between the rate of a reaction and the concentrations of the reactant or reactants. Rate laws are expressions of the relationship between experimentally observed rates and concentrations.

As a second example of a reaction rate, we consider the dimerization reaction of butadiene gas, $CH_2=CH-CH=CH_2$. Two butadiene molecules can combine to form vinylcyclohexene, shown in [\[link\]](#).

Dimerization of Butadiene to Vinylcyclohexene



[\[link\]](#) provides experimental data on the gas phase concentration of butadiene $[C_4H_6]$ as a function of time at $T = 250^\circ C$.

Time (s)	$[C_4H_6]$ (M)	Rate (M/s)	$\frac{\text{Rate}}{[C_4H_6]}$	$\frac{\text{Rate}}{[C_4H_6]^2}$
0	0.0917	9.48×10^{-6}	1.03×10^{-4}	1.13×10^{-3}
500	0.0870	8.55×10^{-6}	9.84×10^{-5}	1.13×10^{-3}
1000	0.0827	7.75×10^{-6}	9.37×10^{-5}	1.13×10^{-3}
1500	0.0788	7.05×10^{-6}	8.95×10^{-5}	1.14×10^{-3}
2000	0.0753	6.45×10^{-6}	8.57×10^{-5}	1.14×10^{-3}
2500	0.0720	5.92×10^{-6}	8.22×10^{-5}	1.14×10^{-3}
3000	0.0691	5.45×10^{-6}	7.90×10^{-5}	1.14×10^{-3}
3500	0.0664	5.04×10^{-6}	7.60×10^{-5}	1.14×10^{-3}

Time (s)	$[C_4H_6]$ (M)	Rate (M/s)	$\frac{\text{Rate}}{[C_4H_6]}$	$\frac{\text{Rate}}{[C_4H_6]^2}$
4000	0.0638	4.67×10^{-6}	7.32×10^{-5}	1.15×10^{-3}

Dimerization of Butadiene at 250°C

We can estimate the rate of reaction at each time step as in [\[link\]](#), and these data are presented in [\[link\]](#) as well. Again we see that the rate of reaction decreases as the concentration of butadiene decreases. This suggests that the rate is given by an expression like [\[link\]](#). To test this, we calculate $\frac{\text{Rate}}{[C_4H_6]}$ in [\[link\]](#) for each time step. We note that this is **not** a constant, so [\[link\]](#) does not describe the relationship between the rate of reaction and the concentration of butadiene. Instead we calculate $\frac{\text{Rate}}{[C_4H_6]^2}$ in [\[link\]](#). We discover that this ratio is a constant throughout the reaction. Therefore, the relationship between the rate of the reaction and the concentration of the reactant in this case is given by

Equation:

$$\begin{aligned}\text{Rate} &= -\frac{d[C_4H_6]}{dt} \\ &= k[C_4H_6]^2\end{aligned}$$

which is the rate law for the reaction in [\[link\]](#). This is a very interesting result when compared to [\[link\]](#). In both cases, the results demonstrate that the rate of reaction depends on the concentration of the reactant. However, we now also know that the way in which the rate varies with the concentration depends on what the reaction is. Each reaction has its own rate law, observed experimentally.

Observation 2: Rate Laws and the Order of Reaction

We would like to understand what determines the specific dependence of the reaction rate on concentration in each reaction. In the first case considered above, the rate depends on the concentration of the reactant to the first power. We refer to this as a **first order reaction**. In the second case above, the rate

depends on the concentration of the reactant to the second power, so this is called a **second order reaction**. There are also **third order reactions**, and even **zeroth order reactions** whose rates do not depend on the amount of the reactant. We need more observations of rate laws for different reactions.

The approach used in the [previous section](#) to determine a reaction's rate law is fairly clumsy and at this point difficult to apply. We consider here a more systematic approach. First, consider the decomposition of $N_2O_5(g)$.



We can create an initial concentration of N_2O_5 in a flask and measure the rate at which the N_2O_5 first decomposes. We can then create a different initial concentration of N_2O_5 and measure the new rate at which the N_2O_5 decomposes. By comparing these rates, we can find the order of the decomposition reaction. The rate law for decomposition of $N_2O_5(g)$ is of the general form:

Equation:

$$\text{Rate} = k[N_2O_5]^m$$

so we need to determine the exponent m . For example, at $25^\circ C$ we observe that the rate of decomposition is $1.4 \times 10^{-3} \frac{M}{s}$ when the concentration of N_2O_5 is $0.020M$. If instead we begin we $[N_2O_5] = 0.010M$, we observe that the rate of decomposition is $7.0 \times 10^{-4} \frac{M}{s}$. We can compare the rate from the first measurement Rate (1) to the rate from the second measurement Rate (2). From [\[link\]](#), we can write that

Equation:

$$\begin{aligned} \frac{\text{Rate (1)}}{\text{Rate (2)}} &= \frac{k[N_2O_5]_1^m}{k[N_2O_5]_2^m} \\ &= \frac{1.4 \times 10^{-3} \frac{M}{s}}{7.0 \times 10^{-4} \frac{M}{s}} \\ &= \frac{k(0.020M)^m}{k(0.010M)^m} \end{aligned}$$

This can be simplified on both sides of the equation to give

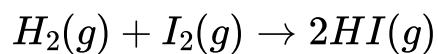
$$2.0 = 2.0^m$$

Clearly, then $m = 1$, and the decomposition is a first order reaction. We can also then find the first order rate constant k for this reaction by simply plugging in one of the initial rate measurements to [\[link\]](#). We find that $k = 0.070s^{-1}$.

This approach to finding reaction order is called the method of initial rates, since it relies on fixing the concentration at specific initial values and measuring the initial rate associated with each concentration.

So far we have considered only reactions which have a single reactant. Consider a second example of the method of initial rates involving the reaction of hydrogen gas and iodine gas:

Equation:



In this case, we expect to find that the rate of the reaction depends on the concentrations for both reactants. As such, we need more initial rate observations to determine the rate law. In [\[link\]](#), observations are reported for the initial rate for three sets of initial concentrations of H_2 and I_2 .

Experiment	$[H_2]_0$ (M)	$[I_2]_0$ (M)	Rate (M/sec)
1	0.10	0.10	3.00×10^{-4}
2	0.20	0.10	6.00×10^{-4}
3	0.20	0.20	1.19×10^{-3}

Hydrogen Gas and Iodine Gas Initial Rate Data at 700K

Following the same process we used in the N_2O_5 example, we write the general rate law for the reaction as

Equation:

$$\text{Rate} = k[H_2]^n[I_2]^m$$

By comparing experiment 1 to experiment 2, we can write

Equation:

$$\begin{aligned}\frac{\text{Rate (1)}}{\text{Rate (2)}} &= \frac{k[H_2]_1^n[I_2]_1^m}{k[H_2]_2^n[I_2]_2^m} \\ &= \frac{3.00 \times 10^{-4} \frac{M}{s}}{6.00 \times 10^{-4} \frac{M}{s}} \\ &= \frac{k(0.10M)^m(0.10M)^n}{k(0.20M)^m(0.10M)^n}\end{aligned}$$

This simplifies to

$$0.50 = 0.50^m 1.00^n$$

from which it is clear that $m = 1$. Similarly, we can find that $n = 1$. The reaction is therefore first order in each reactant and is second order overall.

Equation:

$$\text{Rate} = k[H_2][I_2]$$

Once we know the rate law, we can use any of the data from [\[link\]](#) to determine the rate constant, simply by plugging in concentrations and rate into [\[link\]](#). We find that $k = 3.00 \times 10^{-2} \times \frac{1}{Ms}$.

This procedure can be applied to any number of reactions. The challenge is preparing the initial conditions and measuring the initial change in concentration precisely versus time. [\[link\]](#) provides an overview of the rate laws for several reactions. A variety of reaction orders are observed, and they cannot be easily correlated with the stoichiometry of the reaction.

Reaction	Rate Law
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$\text{Rate} = k[NO]^2 [O_2]$
$2NO(g) + 2H_2(g) \rightarrow 2N_2(g) + 2H_2O(g)$	$\text{Rate} = k[NO]^2 [H_2]$
$2ICl(g) + H_2(g) \rightarrow 2HI(g) + I_2(g)$	$\text{Rate} = k [ICl] [H_2]$
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	$\text{Rate} = k [N_2O_5]$
$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$	$\text{Rate} = k [NO_2] [F_2]$
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$	$\text{Rate} = k [H_2O_2]$
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$	$\text{Rate} = k [H_2][Br_2]^{\frac{1}{2}}$
$O_3(g) + Cl(g) \rightarrow O_2(g) + ClO(g)$	$\text{Rate} = k [O_3] [Cl]$

Rate Laws for Various Reactions

Concentrations as a Function of Time and the Reaction Half-life

Once we know the rate law for a reaction, we should be able to predict how fast a reaction will proceed. From this, we should also be able to predict how much reactant remains or how much product has been produced at any given time in the reaction. We will focus on the reactions with a single reactant to illustrate these ideas.

Consider a first order reaction like $A \rightarrow \text{products}$, for which the rate law must be

Equation:

$$\begin{aligned} \text{Rate} &= -\frac{d[A]}{dt} \\ &= k[A] \end{aligned}$$

From Calculus, it is possible to use [\[link\]](#) to find the function $[A](t)$ which tells us the concentration $[A]$ as a function of time. The result is

Equation:

$$[A] = [A]_0 e^{-(kt)}$$

or equivalently

Equation:

$$\ln([A]) = \ln([A]_0) - kt$$

[\[link\]](#) reveals that, if a reaction is first order, we can plot $\ln([A])$ versus time and get a straight line with slope equal to $-k$. Moreover, if we know the rate constant and the initial concentration, we can predict the concentration at any time during the reaction.

An interesting point in the reaction is the time at which exactly half of the original concentration of A has been consumed. We call this time the **half life** of the reaction and denote it as $t_{\frac{1}{2}}$. At that time, $[A] = \frac{1}{2}[A]_0$. From [\[link\]](#) and using the properties of logarithms, we find that, for a first order reaction

Equation:

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$$

This equation tells us that the half-life of a first order reaction does not depend on how much material we start with. It takes exactly the same amount of time for the reaction to proceed from all of the starting material to half of the starting material as it does to proceed from half of the starting material to one-fourth of the starting material. In each case, we halve the remaining material in a time equal to the constant half-life in [\[link\]](#).

These conclusions are only valid for first order reactions. Consider then a second order reaction, such as the butadiene dimerization discussed [above](#). The general second order reaction $A \rightarrow \text{products}$ has the rate law

Equation:

$$\begin{aligned}\text{Rate} &= -\frac{d[A]}{dt} \\ &= k[A]^2\end{aligned}$$

Again, we can use Calculus to find the function $[A](t)$ from [\[link\]](#). The result is most easily written as

Equation:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k(t)$$

Note that, as t increases, $\frac{1}{[A]}$ increases, so $[A]$ decreases. [\[link\]](#) reveals that, for a reaction which is second order in the reactant A , we can plot $\frac{1}{[A]}$ as a function of time to get a straight line with slope equal to k . Again, if we know the rate constant and the initial concentration, we can find the concentration $[A]$ at any time of interest during the reaction.

The half-life of a second order reaction differs from the half-life of a first order reaction. From [\[link\]](#), if we take $[A] = \frac{1}{2}[A]_0$, we get

Equation:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

This shows that, unlike a first order reaction, the half-life for a second order reaction depends on how much material we start with. From [\[link\]](#), the more concentrated the reactant is, the shorter the half-life.

Observation 3: Temperature Dependence of Reaction Rates

It is a common observation that reactions tend to proceed more rapidly with increasing temperature. Similarly, cooling reactants can have the effect of

slowing a reaction to a near halt. How is this change in rate reflected in the rate law equation, e.g. [\[link\]](#)? One possibility is that there is a slight dependence on temperature of the concentrations, since volumes do vary with temperature. However, this is insufficient to account for the dramatic changes in rate typically observed. Therefore, the temperature dependence of reaction rate is primarily found in the rate constant, k .

Consider for example the reaction of hydrogen gas with iodine gas at high temperatures, as given in [\[link\]](#). The rate constant of this reaction at each temperature can be found using the method of initial rates, as discussed above, and we find in [\[link\]](#) that the rate constant increases dramatically as the temperature increases.

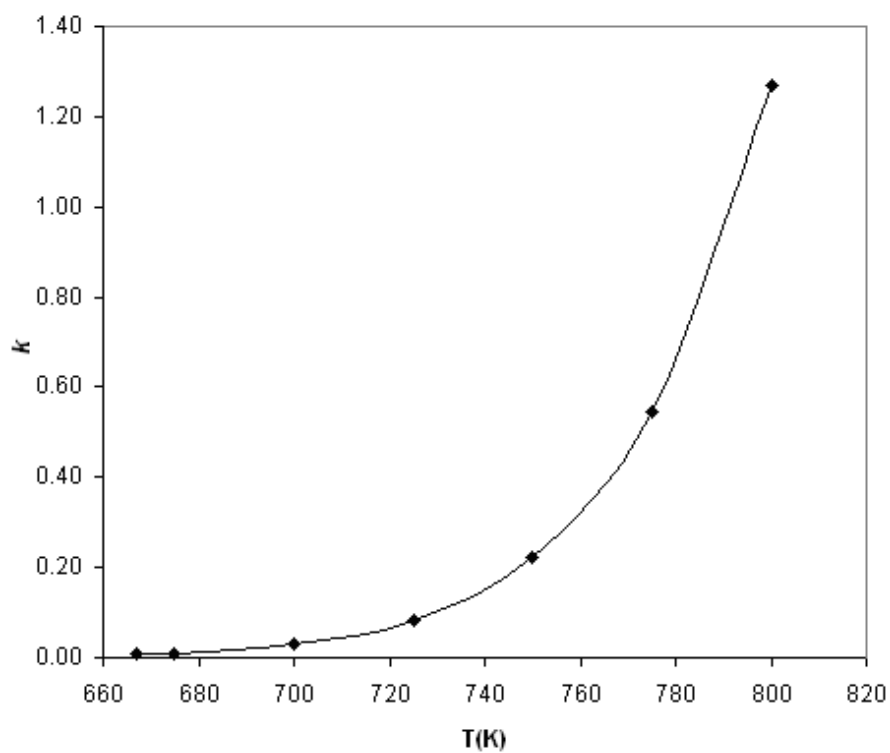
T (K)	$k \left(\frac{1}{Ms} \right)$
667	6.80×10^{-3}
675	9.87×10^{-3}
700	3.00×10^{-2}
725	8.43×10^{-2}
750	2.21×10^{-1}
775	5.46×10^{-1}
800	1.27

Rate Constant for Hydrogen Gas and Iodine Gas

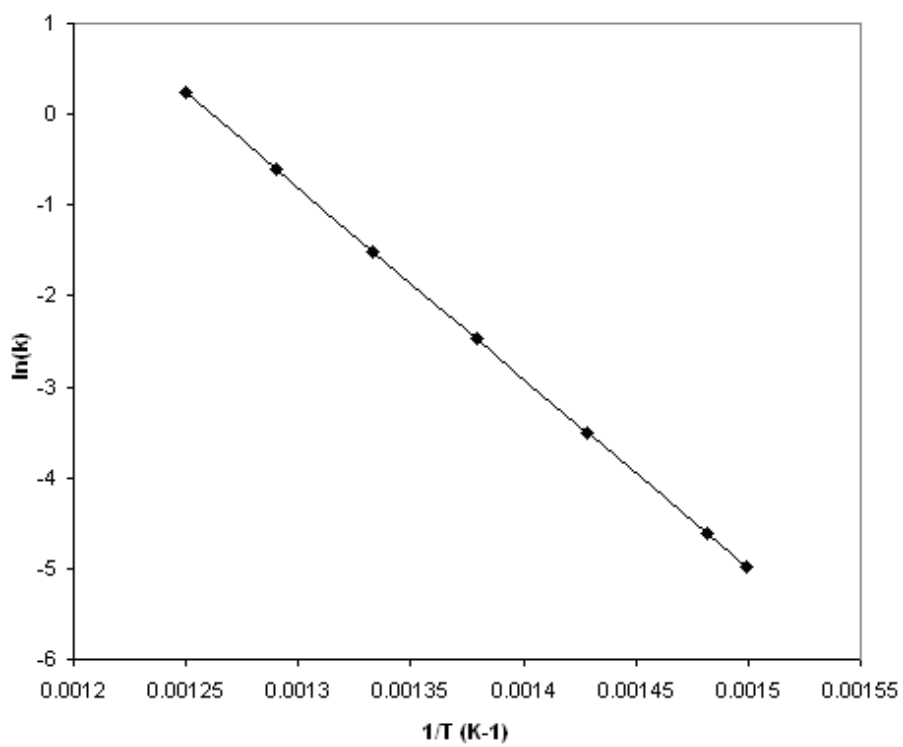
As shown in [\[link\]](#), the rate constant appears to increase exponentially with temperature. After a little experimentation with the data, we find in [\[link\]](#)

that there is a simple linear relationship between $\ln(k)$ and $\frac{1}{T}$.

Rate Constant



Rate Constant



From [\[link\]](#), we can see that the data in [\[link\]](#) fit the equation

Equation:

$$\ln(k) = a \frac{1}{T} + b$$

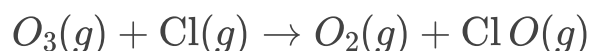
where a and b are constant for this reaction. It turns out that, for our purposes, all reactions have rate constants which fit [\[link\]](#), but with different constants a and b for each reaction. [\[link\]](#) is referred to as an **Arrhenius plot**, after Svante Arrhenius.

It is very important to note that the form of [\[link\]](#) and the appearance of [\[link\]](#) are both the same as the equations and graphs for the temperature dependence of the equilibrium constant for an endothermic reaction. This suggests a model to account for the temperature dependence of the rate constant, based on the energetics of the reaction. In particular, it appears that the reaction rate is related to the amount of energy required for the reaction to occur. We will develop this further in the next section.

Collision Model for Reaction Rates

At this point, we have only observed the dependence of reaction rates on concentration of reactants and on temperature, and we have fit these data to equations called rate laws. Although this is very convenient, it does not provide us insight into why a particular reaction has a specific rate law or why the temperature dependence should obey [\[link\]](#). Nor does it provide any physical insights into the order of the reaction or the meaning of the constants a and b in [\[link\]](#).

We begin by asking why the reaction rate should depend on the concentration of the reactants. To answer this, we consider a simple reaction between two molecules in which atoms are transferred between the molecules during the reaction. For example, a reaction important in the decomposition of ozone O_3 by aerosols is



What must happen for a reaction to occur between an O_3 molecule and a Cl atom? Obviously, for these two particles to react, they must come into close proximity to one another so that an O atom can be transferred from one to the other. In general, two molecules cannot trade atoms to produce new product molecules unless they are close enough together for the atoms of the two molecules to interact. This requires a collision between molecules.

The rate of collisions depends on the concentrations of the reactants, since the more molecules there are in a confined space, the more likely they are to run into each other. To write this relationship in an equation, we can think in terms of probability, and we consider the reaction above. The probability for an O_3 molecule to be near a specific point increases with the number of O_3 molecules, and therefore increases with the concentration of O_3 molecules. The probability for a Cl atom to be near that specific point is also proportional to the concentration of Cl atoms. Therefore, the probability for an O_3 molecule and a Cl atom to be in close proximity to the same specific point at the same time is proportional to the $[O_3]$ times $[Cl]$.

It is important to remember that not all collisions between O_3 molecules and Cl atoms will result in a reaction. There are other factors to consider including how the molecules approach one another. The atoms may not be positioned properly to exchange between molecules, in which case the molecules will simply bounce off of one another without reacting. For example, if the Cl atom approaches the center O atom of the O_3 molecule, that O atom will not transfer. Another factor is energy associated with the reaction. Clearly, though, a collision must occur for the reaction to occur, and therefore the rate of the reaction can be no faster than the rate of collisions between the reactant molecules.

Therefore, we can say that, in a **bimolecular reaction**, where two molecules collide and react, the rate of the reaction will be proportional to the product of the concentrations of the reactants. For the reaction of O_3 with Cl, the rate must therefore be proportional to $[O_3] [Cl]$, and we observe this in the experimental rate law in [\[link\]](#). Thus, it appears that we can understand the rate law by understanding the collisions which must occur for the reaction to take place.

We also need our model to account for the temperature dependence of the rate constant. As noted at the end of the [last section](#), the temperature dependence of the rate constant in [\[link\]](#) is the same as the temperature dependence of the equilibrium constant for an endothermic reaction. This suggests that the temperature dependence is due to an energetic factor required for the reaction to occur. However, we find experimentally that [\[link\]](#) describes the rate constant temperature dependence regardless of whether the reaction is endothermic or exothermic. Therefore, whatever the energetic factor is that is required for the reaction to occur, it is not just the endothermicity of the reaction. It must be that all reactions, regardless of the overall change in energy, require energy to occur.

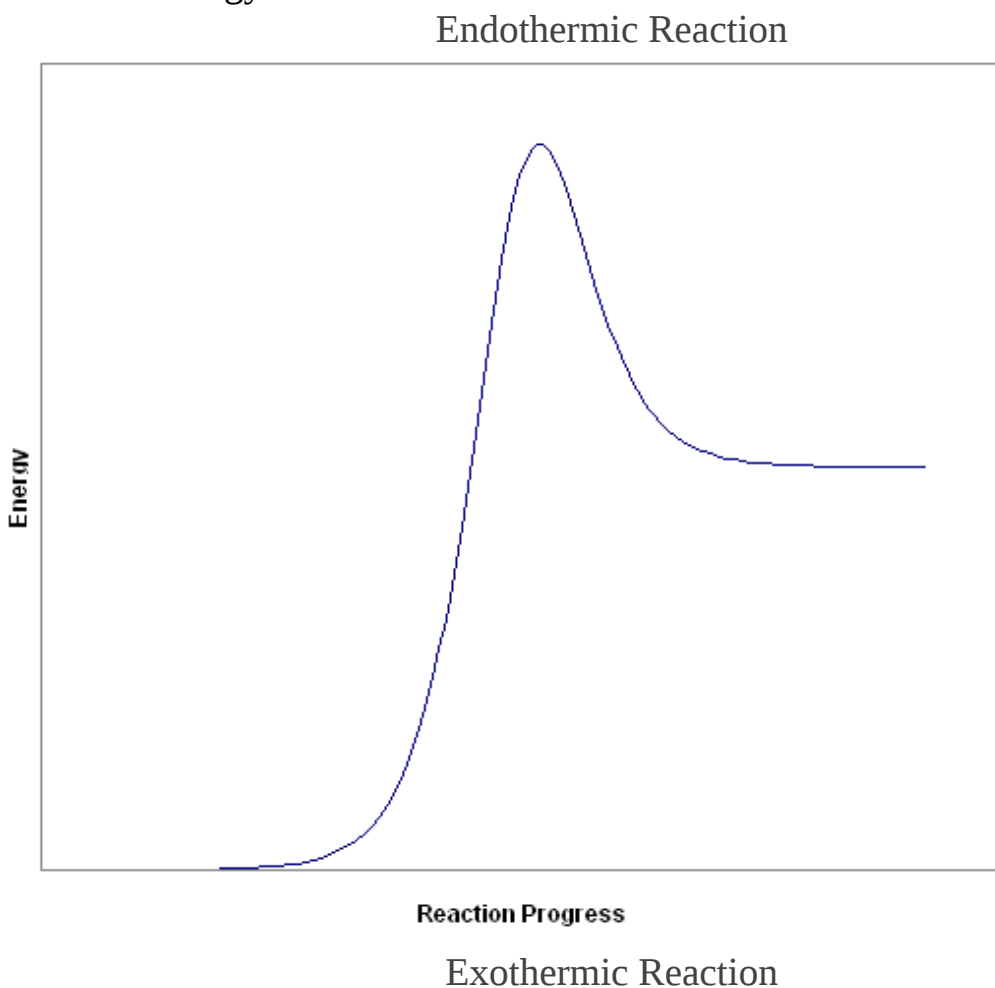
A model to account for this is the concept of **activation energy**. For a reaction to occur, at least some bonds in the reactant molecule must be broken, so that atoms can rearrange and new bonds can be created. At the time of collision, bonds are stretched and broken as new bonds are made. Breaking these bonds and rearranging the atoms during the collision requires the input of energy. The minimum amount of energy required for the reaction to occur is called the activation energy, E_a . This is illustrated in [\[link\]](#), showing conceptually how the energy of the reactants varies as the reaction proceeds. In [\[link\]](#), the energy is low early in the reaction, when the molecules are still arranged as reactants. As the molecules approach and begin to rearrange, the energy rises sharply, rising to a maximum in the middle of the reaction. This sharp rise in energy is the activation energy, as illustrated. After the middle of the reaction has passed and the molecules are arranged more as products than reactants, the energy begins to fall again. However, the energy does not fall to its original value, so this is an endothermic reaction.

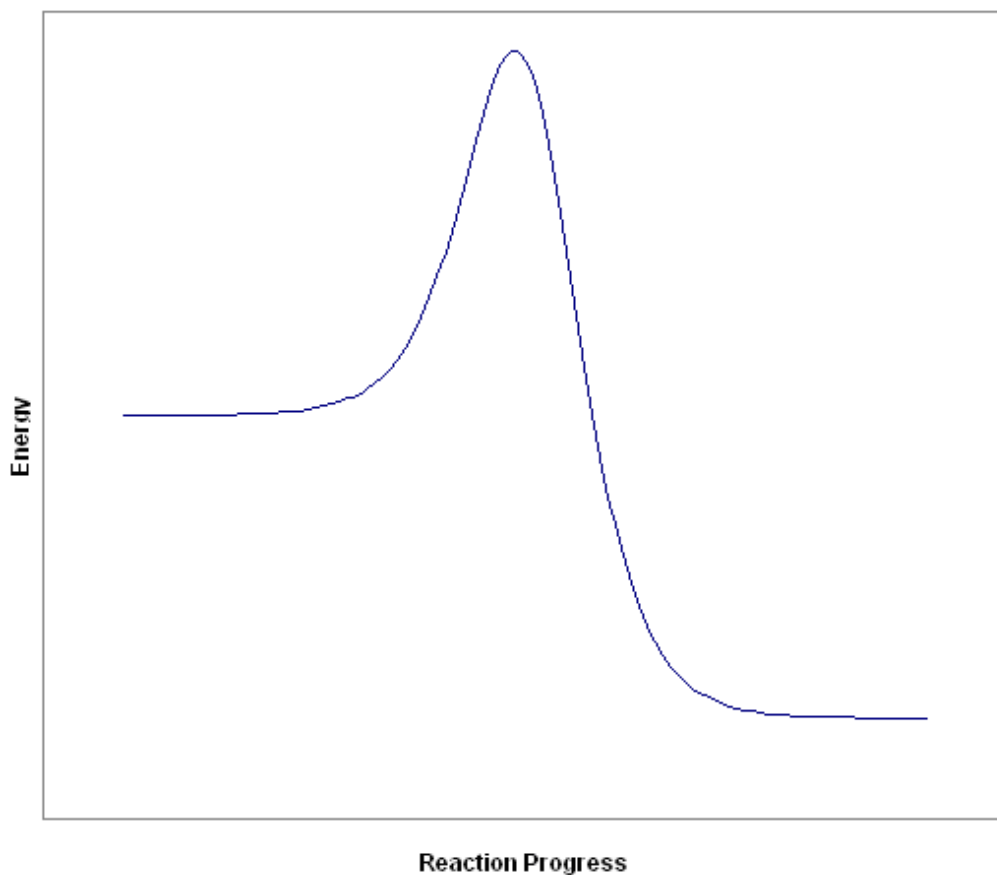
[\[link\]](#) shows the analogous situation for an exothermic reaction. Again, as the reactants approach one another, the energy rises as the atoms begin to rearrange. At the middle of the collision, the energy maximizes and then falls as the product molecules form. In an exothermic reaction, the product energy is lower than the reactant energy.

[\[link\]](#) thus shows that an energy barrier must be surmounted for the reaction to occur, regardless of whether the energy of the products is greater than ([\[link\]](#)) or less than ([\[link\]](#)) the energy of the reactants. This barrier accounts

for the temperature dependence of the reaction rate. We know from the kinetic molecular theory that as temperature increases the average energy of the molecules in a sample increases. Therefore, as temperature increases, the fraction of molecules with sufficient energy to surmount the reaction activation barrier increases.

Reaction Energy





Although we will not show it here, kinetic molecular theory shows that the fraction of molecules with energy greater than E_a at temperature T is proportional to $e^{-\frac{E_a}{RT}}$. This means that the reaction rate and therefore also the rate constant must be proportional to $e^{-\frac{E_a}{RT}}$. Therefore we can write

Equation:

$$k(T) = Ae^{-\frac{E_a}{RT}}$$

where A is a proportionality constant. If we take the logarithm of both sides of [\[link\]](#), we find that

Equation:

$$\ln(k(T)) = -\frac{E_a}{RT} + \ln(A)$$

This equation matches the experimentally observed [\[link\]](#). We recall that a graph of $\ln(k)$ versus $\frac{1}{T}$ is observed to be linear. Now we can see that the slope of that graph is equal to $-\frac{E_a}{R}$.

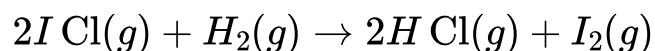
As a final note on [\[link\]](#), the constant A must have some physical significance. We have accounted for the probability of collision between two molecules and we have accounted for the energetic requirement for a successful reactive collision. We have not accounted for the probability that a collision will have the appropriate orientation of reactant molecules during the collision. Moreover, not every collision which occurs with proper orientation and sufficient energy will actually result in a reaction. There are other random factors relating to the internal structure of each molecule at the instant of collision. The factor A takes account for all of these factors, and is essentially the probability that a collision with sufficient energy for reaction will indeed lead to reaction. A is commonly called the **frequency factor**.

Observation 4: Rate Laws for More Complicated Reaction Processes

Our collision model in the previous section accounts for the concentration and temperature dependence of the reaction rate, as expressed by the rate law. The concentration dependence arises from calculating the probability of the reactant molecules being in the same vicinity at the same instant. Therefore, we should be able to predict the rate law for any reaction by simply multiplying together the concentrations of all reactant molecules in the balanced stoichiometric equation. The order of the reaction should therefore be simply related to the stoichiometric coefficients in the reaction. However, [\[link\]](#) shows that this is incorrect for many reactions.

Consider for example the apparently simple reaction

Equation:



Based on the collision model, we would assume that the reaction occurs by $2I\ Cl$ molecules colliding with a single H_2 molecule. The probability for

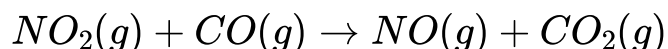
such a collision should be proportional to $[I\ Cl]^2 [H_2]$. However, experimentally we observe (see [\[link\]](#)) that the rate law for this reaction is

Equation:

$$\text{Rate} = k [I\ Cl] [H_2]$$

As a second example, consider the reaction

Equation:



It would seem reasonable to assume that this reaction occurs as a single collision in which an oxygen atom is exchanged between the two molecules. However, the experimentally observed rate law for this reaction is

Equation:

$$\text{Rate} = k[NO_2]^2$$

In this case, the $[CO]$ concentration does not affect the rate of the reaction at all, and the $[NO_2]$ concentration is squared. These examples demonstrate that the rate law for a reaction cannot be predicted from the stoichiometric coefficients and therefore that the collision model does not account for the rate of the reaction. There must be something seriously incomplete with the collision model.

The key assumption of the collision model is that the reaction occurs by a single collision. Since this assumption leads to incorrect predictions of rate laws in some cases, the assumption must be invalid in at least those cases. It may well be that reactions require more than a single collision to occur, even in reactions involving just two types of molecules as in [\[link\]](#). Moreover, if more than two molecules are involved as in [\[link\]](#), the chance of a single collision involving all of the reactive molecules becomes very small. We conclude that many reactions, including those in [\[link\]](#) and [\[link\]](#), must occur as a result of several collisions occurring in sequence, rather than a single collision. The rate of the chemical reaction must be determined by the rates of the individual steps in the reaction.

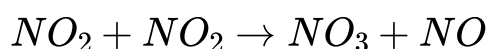
Each step in a complex reaction is a single collision, often referred to as an **elementary process**. In single collision process step, our collision model should correctly predict the rate of that step. The sequence of such elementary processes leading to the overall reaction is referred to as the **reaction mechanism**. Determining the mechanism for a reaction can require gaining substantially more information than simply the rate data we have considered here. However, we can gain some progress just from the rate law.

Consider for example the reaction in [\[link\]](#) described by the rate law in [\[link\]](#). Since the rate law involved $[NO_2]^2$, one step in the reaction mechanism must involve the collision of two NO_2 molecules. Furthermore, this step must determine the rate of the overall reaction. Why would that be? In any multi-step process, if one step is considerably slower than all of the other steps, the rate of the multi-step process is determined entirely by that slowest step, because the overall process cannot go any faster than the slowest step. It does not matter how rapidly the rapid steps occur. Therefore, the slowest step in a multi-step process is thus called the **rate determining** or **rate limiting** step.

This argument suggests that the reaction in [\[link\]](#) proceeds via a slow step in which two NO_2 molecules collide, followed by at least one other rapid step leading to the products. A possible mechanism is therefore

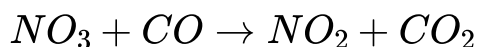
Equation:

Step 1



Equation:

Step 2



If [Step 1](#) is much slower than [Step 2](#), the rate of the reaction is entirely determined by the rate of [Step 1](#). From our collision model, the rate law for [Step 1](#) must be $\text{Rate} = k[NO_2]^2$, which is consistent with the experimentally observed rate law for the overall reaction. This suggests that the mechanism in [\[link\]](#) and [\[link\]](#) is the correct description of the reaction process for [\[link\]](#), with the first step as the rate determining step.

There are a few important notes about the mechanism. First, one product of the reaction is produced in the first step, and the other is produced in the second step. Therefore, the mechanism does lead to the overall reaction, consuming the correct amount of reactant and producing the correct amount of reactant. Second, the first reaction produces a new molecule, NO_3 , which is neither a reactant nor a product. The second step then consumes that molecule, and NO_3 therefore does not appear in the overall reaction, [\[link\]](#). As such, NO_3 is called a **reaction intermediate**. Intermediates play important roles in the rates of many reactions.

If the first step in a mechanism is rate determining as in this case, it is easy to find the rate law for the overall expression from the mechanism. If the second step or later steps are rate determining, determining the rate law is slightly more involved. The process for finding the rate law in such a case is illustrated in [\[link\]](#).

Review and Discussion Questions

Exercise:

Problem:

When $C_{60}O_3$ in toluene solution decomposes, O_2 is released leaving $C_{60}O$ in solution.

Based on the data in [\[link\]](#) and [\[link\]](#), plot the concentration of $C_{60}O$ as a function of time.

How would you define the rate of the reaction in terms of the slope of the graph from [above](#)? How is the rate of appearance of $C_{60}O$ related to the rate of disappearance of $C_{60}O_3$? Based on this, plot the rate of appearance of $C_{60}O$ as a function of time.

Exercise:

Problem:

The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ was found in this study to have rate law given by $\text{Rate} = k[N_2O_5]$ with $k = 0.070s^{-1}$.

How is the rate of appearance of NO_2 related to the rate of disappearance of N_2O_5 ? Which rate is larger?

Based on the rate law and rate constant, sketch a plot of $[N_2O_5]$, $[NO_2]$, and $[O_2]$ versus time all on the same graph.

Exercise:

Problem:

For which of the reactions listed in [\[link\]](#) can you be certain that the reaction does not occur as a single step collision? Explain your reasoning.

Exercise:

Problem:

Consider two decomposition reactions for two hypothetical materials, A and B. The decomposition of A is found to be first order, and the decomposition of B is found to be second order.

Assuming that the two reactions have the same rate constant at the same temperature, sketch $[A]$ and $[B]$ versus time on the same graph for the same initial conditions, i.e. $[A]_0 = [B]_0$.

Compare the half-lives of the two reactions. Under what conditions will the half-life of B be less than the half-life of A? Under what conditions will the half-life of B be greater than the half-life of A?

Exercise:

Problem:

A graph of the logarithm of the equilibrium constant for a reaction versus $\frac{1}{T}$ is linear but can have either a negative slope or a positive slope, depending on the reaction, as was observed [here](#). However, the graph of the logarithm of the rate constant for a reaction versus $\frac{1}{T}$ has a negative slope for essentially every reaction. Using equilibrium arguments, explain why the graph for the rate constant must have a negative slope.

Exercise:

Problem:

Using [\[link\]](#) and the data in [\[link\]](#), determine the activation energy for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$.

Exercise:

Problem:

We found that the rate law for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ is $\text{Rate} = k [H_2] [I_2]$. Therefore, the reaction is **second order** overall but **first order** in H_2 . Imagine that we start with $[H_2]_0 = [I_2]_0$ and we measure $[H_2]$ versus time. Will a graph of $\ln([H_2])$ versus time be linear or will a graph of $\frac{1}{[H_2]}$ versus time be linear? Explain your reasoning.

Exercise:

Problem:

As a rough estimate, chemists often assume a **rule of thumb** that the rate of any reaction will double when the temperature is increased by $10^\circ C$.

What does this suggest about the activation energies of reactions?

Using [\[link\]](#), calculate the activation energy of a reaction whose rate doubles when the temperature is raised from $25^\circ C$ to $35^\circ C$.

Does this rule of thumb estimate depend on the temperature range? To find out, calculate the factor by which the rate constant increases when the temperature is raised from 100°C to 110°C , assuming the same activation energy you found [above](#). Does the rate double in this case?

Exercise:

Problem:

Consider a very simple hypothetical reaction $A + B \leftrightarrow 2C$ which comes to equilibrium.

At equilibrium, what must be the relationship between the rate of the forward reaction, $A + B \rightarrow 2C$ and the reverse reaction $2C \rightarrow A + B$?

Assume that both the forward and reverse reactions are elementary processes occurring by a single collision. What is the rate law for the forward reaction? What is the rate law for the reverse reaction?

Using the previous results from [here](#) and [here](#), show that the equilibrium constant for this reaction can be calculated from $K_c = \frac{k_f}{k_r}$, where k_f is the rate constant for the forward reaction and k_r is the rate constant for the reverse reaction.

Exercise:

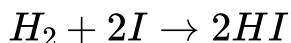
Problem:

Consider a very simple hypothetical reaction $A + B \leftrightarrow C + D$. By examining [\[link\]](#), provide and explain the relationship between the activation energy in the forward direction, $E_{a,f}$, and in the reverse direction, $E_{a,r}$. Does this relationship depend on whether the reaction is endothermic ([\[link\]](#)) or exothermic ([\[link\]](#))? Explain.

Exercise:

Problem:

For the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$, the rate law is $\text{Rate} = k [H_2] [I_2]$. Although this suggests that the reaction is a one-step elementary process, there is evidence that the reaction occurs in two steps, and the second step is the rate determining step:

Equation:**Step 1****Equation:****Step 2**

Where [Step 1](#) is fast and [Step 2](#) is slow.

If the both the forward and reverse reactions in [Step 1](#) are much faster than [Step 2](#), explain why [Step 1](#) can be considered to be at equilibrium.

What is the rate law for the rate determining step?

Since the rate law [above](#) depends on the concentration of an intermediate I , we need to find that intermediate. Calculate $[I]$ from [Step 1](#), assuming that [Step 1](#) is at equilibrium.

Substitute $[I]$ from [above](#) into the rate law found [previously](#) to find the overall rate law for the reaction. Is this result consistent with the experimental observation?

Equilibrium and the Second Law of Thermodynamics

Foundation

We have observed and defined phase transitions and phase equilibrium. We have also observed equilibrium in a variety of reaction systems. We will assume an understanding of the postulates of the **Kinetic Molecular Theory** and of the energetics of chemical reactions.

Goals

We have developed an understanding of the concept of equilibrium, both for phase equilibrium and reaction equilibrium. As an illustration, at normal atmospheric pressure, we expect to find H_2O in solid form below 0°C , in liquid form below 100°C , and in gaseous form above 100°C . What changes as we move from low temperature to high temperature cause these transitions in which phase is observed? Viewed differently, if a sample of gaseous water at 120°C is cooled to below 100°C , virtually all of the water vapor spontaneously condenses to form the liquid:

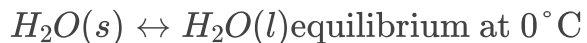


By contrast, very little of liquid water at 80°C spontaneously converts to gaseous water:



We can thus rephrase our question as, what determines which processes are spontaneous and which are not? What factors determine what phase is "stable"?

As we know, at certain temperatures and pressures, more than one phase can be stable. For example, at 1 atm pressure and 0°C ,



Small variations in the amount of heat applied or extracted to the liquid-solid equilibrium cause shifts towards liquid or solid without changing the temperature of the two phases at equilibrium. Therefore, when the two phases are at equilibrium, neither direction of the phase transition is spontaneous at 0°C . We therefore need to understand what factors determine when two or more phases can co-exist at equilibrium.

This analysis leaves unanswered a series of questions regarding the differences between liquids and gases. The concept of a gas phase or a liquid phase is not a characteristic of an individual molecule. In fact, it does not make any sense to refer to the "phase" of an individual molecule. The phase is a collective property of large numbers of molecules.

Although we can discuss the importance of molecular properties regarding liquid and gas phases, we have not discussed the factors which determine whether the gas phase or the liquid phase is most stable at a given temperature and pressure.

These same questions can be applied to reaction equilibrium. When a mixture of reactants and products is not at equilibrium, the reaction will occur spontaneously in one direction or the other until the reaction achieves equilibrium. What determines the direction of spontaneity? What is the driving force towards equilibrium? How does the system **know** that equilibrium has been achieved? Our goal will be to understand the driving forces behind spontaneous processes and the determination of the equilibrium point, both for phase equilibrium and reaction equilibrium.

Observation 1: Spontaneous Mixing

We begin by examining common characteristics of spontaneous processes, and for simplicity, we focus on processes not involving phase transitions or chemical reactions. A very clear example of such a process is mixing. Imagine putting a drop of blue ink in a glass of water. At first, the blue dye in the ink is highly concentrated. Therefore, the molecules of the dye are closely congregated. Slowly but steadily, the dye begins to diffuse throughout the entire glass of water, so that eventually the water appears as a uniform blue color. This occurs more readily with agitation or stirring but occurs spontaneously even without such effort. Careful measurements show that this process occurs without a change in temperature, so there is no energy input or released during the mixing.

We conclude that, although there is no energetic advantage to the dye molecules dispersing themselves, they do so spontaneously. Furthermore, this process is **irreversible** in the sense that, without considerable effort on our part, the dye molecules will never return to form a single localized drop. We now seek an understanding of how and why this mixing occurs.

Consider the following rather abstract model for the dye molecules in the water. For the glass, we take a row of ten small boxes, each one of which represents a possible location for a molecule, either of water or of dye. For the molecules, we take marbles, clear for water and blue for ink. Each box will accommodate only a single marble, since two molecules cannot be in the same place at the same time. Since we see a drop of dye when the molecules are congregated, we model a "drop" as three blue marbles in consecutive boxes. Notice that there are only eight ways to have a "drop" of dye, assuming that the three dye "molecules" are indistinguishable from one another. Two possibilities are shown in [\[link\]](#) and [\[link\]](#). It is not difficult to find the other six.

Arrangement of Three Ink Molecules



An unmixed state.



Another unmixed state.



A mixed state.



Another mixed state.

By contrast, there are many more ways to arrange the dye molecules so that they do not form a drop, i.e., so that the three molecules are not together. Two possibilities are shown in [\[link\]](#) and [\[link\]](#). The total number of such possibilities is 112. (The total number of all possible arrangements can be calculated as follows: there are 10 possible locations for the first blue marble, 9 for the second, and 8 for the third. This gives 720 possible arrangements, but many of these are identical, since the marbles are indistinguishable. The number of duplicates for each arrangement is 6, calculated from three choices for the first marble, two for the second, and one for the third. The total number of non-identical arrangements of the molecules is $\frac{720}{6} = 120$.) We conclude that, if we randomly place the 3 marbles in the tray of 10 boxes, the chances are only 8 out of 120 (or 1 out of 15) of observing a drop of ink.

Now, in a real experiment, there are many, many times more ink molecules and many, many times more possible positions for each molecule. To see how this comes into play, consider a row of 500 boxes and 5 blue marbles. (The **mole fraction** of ink is thus 0.01.) The total number of distinct configurations of the blue marbles in these boxes is approximately 2×10^{11} . The number of these configurations which have all five ink marbles together in a drop is 496. If the arrangements are sampled randomly, the chances of observing a drop of ink with all five molecules together are thus about one in 500 million. The possibilities are remote even for observing a partial "droplet"

consisting of fewer than all five dye molecules. The chance for four of the molecules to be found together is about one in 800,000. Even if we define a droplet to be only three molecules together, the chances of observing one are less than one in 1600.

We could, with some difficulty, calculate the probability for observing a drop of ink when there are 10^{23} molecules. However, it is reasonably deduced from our small calculations that the probability is essentially zero for the ink molecules, randomly distributed into the water molecules, to be found together. We conclude from this that the reason why we observe ink to disperse in water is that the probability is infinitesimally small for randomly distributed dye molecules to be congregated in a drop.

Interestingly, however, when we set up the real ink and water experiment, we did not randomly distribute the ink molecules. Rather, we began initially with a drop of ink in which the dye molecules were already congregated. We know that, according to our kinetic theory, the molecules are in constant random motion. Therefore, they must be constantly rearranging themselves. Since these random motions do not energetically favor any one arrangement over any other one arrangement, we can assume that all possible arrangements are equally probable. Since most of the arrangements do not correspond to a drop of ink, then **most of the time** we will not observe a drop. In the case above with five blue marbles in 500 boxes, we expect to see a drop only once in every 500 million times we look at the "glass". In a real glass of water with a real drop of ink, the chances are very much smaller than this.

We draw two very important conclusions from our model. First, the random motions of molecules make every possible arrangement of these molecules equally probable. Second, mixing occurs spontaneously simply because there are vastly many more arrangements which are mixed than which are not. The first conclusion tells us "how" mixing occurs, and the second tells us "why." On the basis of these observations, we deduce the following preliminary generalization: a spontaneous process occurs because it produces the most probable final state.

Probability and Entropy

There is a subtlety in our conclusion to be considered in more detail. We have concluded that all possible arrangements of molecules are equally probable. We have further concluded that mixing occurs because the final mixed state is overwhelmingly probable. Placed together, these statements appear to be openly contradictory. To see why they are not, we must analyze the statements carefully. By an "arrangement" of the molecules, we mean a specification of the location of each and every molecule. We have assumed that, due to random molecular motion, each such arrangement is equally probable. In what sense, then, is the final state "overwhelmingly probable"?

Recall the system illustrated in [\[link\]](#), where we placed three identical blue marbles into ten spaces. We calculated before that there are 120 unique ways to do this. If we ask for the probability of the arrangement in [\[link\]](#), the answer is thus $\frac{1}{120}$. This is also the probability for each of the other possible arrangements, according to our model. However, if we now ask instead for the probability of observing a "mixed" state (with no drop), the answer is $\frac{112}{120}$, whereas the probability of observing an "unmixed" state (with a drop) is only $\frac{8}{120}$. Clearly, the probabilities are not the same when considering the less specific characteristics "mixed" and "unmixed".

In chemistry we are virtually never concerned with **microscopic** details, such as the locations of specific individual molecules. Rather, we are interested in more general characteristics, such as whether a system is mixed or not, or what the temperature or pressure is. These properties of interest to us are **macroscopic**. As such, we refer to a specific arrangement of the molecules as a **microstate**, and each general state (mixed or unmixed, for example) as a **macrostate**. All microstates have the same probability of occurring, according to our model. As such, the macrostates have widely differing probabilities.

We come to an important result: the probability of observing a particular macrostate (e.g., a mixed state) is proportional to the number of microstates with that macroscopic property. For example, from [\[link\]](#), there are 112 arrangements (microstates) with the "mixed" macroscopic property. As we have discussed, the probability of observing a mixed state is $\frac{112}{120}$, which is obviously proportional to 112. Thus, one way to measure the relative probability of a particular macrostate is by the number of microstates W corresponding to that macrostate. W stands for "ways", i.e., there are 112 "ways" to get a mixed state in [\[link\]](#).

Now we recall our conclusion that a spontaneous process always produces the outcome with greatest probability. Since W measures this probability for any substance or system of interest, we could predict, using W , whether the process leading from a given initial state to a given final state was spontaneous by simply comparing probabilities for the initial and final states. For reasons described below, we instead define a function of W ,

Equation:

$$S(W) = k \ln(W)$$

called the **entropy**, which can be used to make such predictions about spontaneity. (The k is a proportionality constant which gives S appropriate units for our calculations.) Notice that the more microstates there are, the greater the entropy is. Therefore, a macrostate with a high probability (e.g. a mixed state) has a large entropy. We now modify our previous deduction to say that a spontaneous process produces the final

state of greatest entropy. (Following modifications added below, this statement forms the **Second Law of Thermodynamics**.)

It would seem that we could use W for our calculations and that the definition of the new function S is unnecessary. However, the following reasoning shows that W is not a convenient function for calculations. We consider two identical glasses of water at the same temperature. We expect that the value of any physical property for the water in two glasses is twice the value of that property for a single glass. For example, if the enthalpy of the water in each glass is H_1 , then it follows that the total enthalpy of the water in the two glasses together is $H_{\text{total}} = 2H_1$. Thus, the enthalpy of a system is proportional to the quantity of material in the system: if we double the amount of water, we double the enthalpy. In direct contrast, we consider the calculation involving W for these two glasses of water. The number of microstates of the macroscopic state of one glass of water is W_1 , and likewise the number of microstates in the second glass of water is W_1 . However, if we combine the two glasses of water, the number of microstates of the total system is found from the product $W_{\text{total}} = W_1 \times W_1$, which does not equal $2W_1$. In other words, W is not proportional to the quantity of material in the system. This is inconvenient, since the value of W thus depends on whether the two systems are combined or not. (If it is not clear that we should multiply the W values, consider the simple example of rolling dice. The number of states for a single die is 6, but for two dice the number is $6 \times 6 = 36$, not $6 + 6 = 12$.)

We therefore need a new function $S(W)$, so that, when we combine the two glasses of water, $S_{\text{total}} = S_1 + S_1$. Since $S_{\text{total}} = S(W_{\text{total}})$, $S_1 = S(W_1)$, and $W_{\text{total}} = W_1 \times W_1$, then our new function S must satisfy the equation

$$S(W_1 \times W_1) = S(W_1) + S(W_1)$$

The only function S which will satisfy this equation is the logarithm function, which has the property that $\ln(x \times y) = \ln(x) + \ln(y)$. We conclude that an appropriate state function which measures the number of microstates in a particular macrostate is [\[link\]](#).

Observation 2: Absolute Entropies

It is possible, though exceedingly difficult, to calculate the entropy of any system under any conditions of interest from the equation $S = k \ln(W)$. It is also possible, using more advanced theoretical thermodynamics, to determine S experimentally by measuring heat capacities and enthalpies of phase transitions. Values of S determined experimentally, often referred to as "absolute" entropies, have been tabulated for many materials at many temperatures, and a few examples are given in [\[link\]](#). We treat these values as observations and attempt to understand these in the context of [\[link\]](#).

	T (°C)	S ($\frac{J}{\text{mol } ^\circ\text{C}}$)
$H_2O(g)$	25	188.8
$H_2O(l)$	25	69.9
$H_2O(l)$	0	63.3
$H_2O(s)$	0	41.3
$NH_3(g)$	25	192.4
$HN_3(l)$	25	140.6
$HN_3(g)$	25	239.0
$O_2(g)$	25	205.1
$O_2(g)$	50	207.4
$O_2(g)$	100	211.7
$CO(g)$	25	197.7
$CO(g)$	50	200.0
$CO_2(g)$	24	213.7
$CO_2(g)$	50	216.9
$Br_2(l)$	25	152.2
$Br_2(g)$	25	245.5
$I_2(s)$	25	116.1
$I_2(g)$	25	260.7
$Ca F_2(s)$	25	68.9
$Ca Cl_2(s)$	25	104.6

	T (°C)	S ($\frac{J}{mol \cdot ^\circ C}$)
Ca Br ₂ (s)	25	130
C ₈ H ₁₈ (s)	25	361.1

Absolute Entropies of Specific Substances

There are several interesting generalities observed in [\[link\]](#). First, in comparing the entropy of the gaseous form of a substance to either its liquid or solid form at the same temperature, we find that the gas always has a substantially greater entropy. This is easy to understand from [\[link\]](#): the molecules in the gas phase occupy a very much larger volume. There are very many more possible locations for each gas molecule and thus very many more arrangements of the molecules in the gas. It is intuitively clear that W should be larger for a gas, and therefore the entropy of a gas is greater than that of the corresponding liquid or solid.

Second, we observe that the entropy of a liquid is always greater than that of the corresponding solid. This is understandable from our kinetic molecular view of liquids and solids. Although the molecules in the liquid occupy a comparable volume to that of the molecules in the solid, each molecule in the liquid is free to move throughout this entire volume. The molecules in the solid are relatively fixed in location. Therefore, the number of arrangements of molecules in the liquid is significantly greater than that in the solid, so the liquid has greater entropy by [\[link\]](#).

Third, the entropy of a substance increases with increasing temperature. The temperature is, of course, a measure of the average kinetic energy of the molecules. In a solid or liquid, then, increasing the temperature increases the total kinetic energy available to the molecules. The greater the energy, the more ways there are to distribute this energy amongst the molecules. Although we have previously only referred to the range of positions for a molecule as affecting W , the range of energies available for each molecule similarly affects W . As a result, as we increase the total energy of a substance, we increase W and thus the entropy.

Fourth, the entropy of a substance whose molecules contain many atoms is greater than that of a substance composed of smaller molecules. The more atoms there are in a molecule, the more ways there are to arrange those atoms. With greater internal flexibility, W is larger when there are more atoms, so the entropy is greater.

Fifth, the entropy of a substance with a high molecular weight is greater than that of substance with a low molecular weight. This result is a harder to understand, as it arises from the distribution of the momenta of the molecules rather than the positions and energies of the molecules. It is intuitively clear that the number of arrangements of the

molecules is **not** affected by the mass of the molecules. However, even at the same temperature, the range of momenta available for a heavier molecule is greater than for a lighter one. To see why, recall that the momentum of a molecule is $p = mv$ and the kinetic energy is $\text{KE} = \frac{mv^2}{2} = \frac{p^2}{2m}$. Therefore, the maximum momentum available at a fixed total kinetic energy KE is $p = \sqrt{2m \text{KE}}$. Since this is larger for larger mass molecules, the range of momenta is greater for heavier particles, thus increasing W and the entropy.

Observation 3: Condensation and Freezing

We have concluded from our observations of spontaneous mixing that a spontaneous process always produces the final state of greatest probability. A few simple observations reveal that our deduction needs some thoughtful refinement. For example, we have observed that the entropy of liquid water is greater than that of solid water. This makes sense in the context of [\[link\]](#), since the kinetic theory indicates that liquid water has a greater value of W . Nevertheless, we observe that liquid water spontaneously freezes at temperatures below 0°C. This process clearly displays a decrease in entropy and therefore evidently a shift from a more probable state to a less probable state. This appears to contradict directly our conclusion.

Similarly, we expect to find condensation of water droplets from steam when steam is cooled. On days of high humidity, water spontaneously liquefies from the air on cold surfaces such as the outside of a glass of ice water or the window of an air conditioned building. In these cases, the transition from gas to liquid is clearly from a higher entropy phase to a lower entropy phase, which does not seem to follow our reasoning thus far.

Our previous conclusions concerning entropy and probability increases were compelling, however, and we should be reluctant to abandon them. What we have failed to take into consideration is that these phase transitions involve changes of energy and thus heat flow. Condensation of gas to liquid and freezing of liquid to solid both involve evolution of heat. This heat flow is of consequence because our observations also revealed that the entropy of a substance can be increased significantly by heating. One way to preserve our conclusions about spontaneity and entropy is to place a condition on their validity: a spontaneous process produces the final state of greatest probability and entropy **provided that** the process does not involve evolution of heat. This is an unsatisfying result, however, since most physical and chemical processes involve heat transfer. As an alternative, we can force the process not to evolve heat by **isolating** the system undergoing the process: no heat can be released if there is no sink to receive the heat, and no heat can be absorbed if there is no source of heat. Therefore, we conclude from our observations that a spontaneous process **in an**

isolated system produces the final state of greatest probability and entropy. This is one statement of the **Second Law of Thermodynamics**.

Free Energy

How can the Second Law be applied to a process in a system that is not isolated? One way to view the lessons of the previous observations is as follows: in analyzing a process to understand why it is or is not spontaneous, we must consider both the change in entropy of the system undergoing the process **and** the effect of the heat released or absorbed during the process on the entropy of the surroundings. Although we cannot prove it here, the entropy increase of a substance due to heat q at temperature T is given by $\Delta(S) = \frac{q}{T}$. From [another study](#), we can calculate the heat transfer for a process occurring under constant pressure from the enthalpy change, $\Delta(H)$. By conservation of energy, the heat flow into the surroundings must be $-\Delta(H)$. Therefore, the increase in the entropy of the surroundings due to heat transfer must be $\Delta(S_{\text{surr}}) = -\frac{\Delta(H)}{T}$. Notice that, if the reaction is exothermic, $\Delta(H) < 0$ so $\Delta(S_{\text{surr}}) > 0$.

According to our statement of the Second Law, a spontaneous process in an isolated system is always accompanied by an increase in the entropy of the system. If we want to apply this statement to a non-isolated system, we must include the surroundings in our entropy calculation. We can say then that, for a spontaneous process,

$$\Delta(S_{\text{total}}) = \Delta(S_{\text{sys}}) + \Delta(S_{\text{surr}}) > 0$$

Since $\Delta(S_{\text{surr}}) = -\frac{\Delta(H)}{T}$, then we can write that $\Delta(S) - \frac{\Delta(H)}{T} > 0$. This is easily rewritten to state that, for a spontaneous process:

Equation:

$$\Delta(H) - T\Delta(S) < 0$$

[\[link\]](#) is really just a different form of the Second Law of Thermodynamics. However, this form has the advantage that it takes into account the effects on both the system undergoing the process and the surroundings. Thus, this new form can be applied to non-isolated systems.

[\[link\]](#) reveals why the temperature affects the spontaneity of processes. Recall that the condensation of water vapor occurs spontaneously at temperature below 100°C but not above. Condensation is an exothermic process; to see this, consider that the reverse process, evaporation, obviously requires heat input. Therefore $\Delta(H) < 0$ for condensation. However, condensation clearly results in a decrease in entropy, therefore

$\Delta(S) < 0$ also. Examining [\[link\]](#), we can conclude that $\Delta(H) - T\Delta(S) < 0$ will be less than zero for condensation only if the temperature is not too high. At high temperature, the term $-\Delta(S)$, which is positive, becomes larger than $\Delta(H)$, so $\Delta(H) - T\Delta(S) > 0$ for condensation at high temperature. Therefore, condensation only occurs at lower temperatures.

Because of the considerable practical utility of [\[link\]](#) in predicting the spontaneity of physical and chemical processes, it is desirable to simplify the calculation of the quantity on the left side of the inequality. One way to do this is to define a new quantity $G = H - TS$, called the **free energy**. If we calculate from this definition the change in the free energy which occurs during a process at constant temperature, we get

$$\Delta(G) = G_{\text{final}} - G_{\text{initial}} = H_{\text{final}} - TS_{\text{final}} - (H_{\text{initial}} - TS_{\text{initial}}) = \Delta(H) - T\Delta(S)$$

and therefore a simplified statement of the Second Law of Thermodynamics in [\[link\]](#) is that

Equation:

$$\Delta(G) < 0$$

for any spontaneous process. Thus, in any spontaneous process, the free energy of the system decreases. Note that G is a state function, since it is defined in terms of H , T , and S , all of which are state functions. Since G is a state function, then $\Delta(G)$ can be calculated along any convenient path. As such, the methods used to calculate $\Delta(H)$ in [another study](#) can be used just as well to calculate $\Delta(G)$.

Thermodynamic Description of Phase Equilibrium

As we recall, the entropy of vapor is much greater than the entropy of the corresponding amount of liquid. A look back at [\[link\]](#) shows that, at 25°C, the entropy of one mole of liquid water is $69.9 \frac{J}{K}$, whereas the entropy of one mole of water vapor is $188.8 \frac{J}{K}$. Our first thought, based on our understanding of spontaneous processes and entropy, might well be that a mole of liquid water at 25°C should spontaneously convert into a mole of water vapor, since this process would greatly increase the entropy of the water. We know, however, that this does not happen. Liquid water will exist in a closed container at 25°C without spontaneously converting entirely to vapor. What have we left out?

The answer, based on our discussion of free energy, is the energy associated with evaporation. The conversion of one mole of liquid water into one mole of water vapor results in absorption of 44.0 kJ of energy from the surroundings. Recall that this loss of energy from the surroundings results in a significant decrease in entropy of the

surroundings. We can calculate the amount of entropy decrease in the surroundings from $\Delta(S_{\text{surr}}) = -\frac{\Delta(H)}{T}$. At 25°C, this gives $\Delta(S_{\text{surr}}) = \frac{-44.0 \text{ kJ}}{298.15 \text{ K}} = -147.57 \frac{\text{J}}{\text{K}}$ for a single mole. This entropy decrease is greater than the entropy increase of the water, $188.8 \frac{\text{J}}{\text{K}} - 69.9 \frac{\text{J}}{\text{K}} = 118.9 \frac{\text{J}}{\text{K}}$. Therefore, the entropy of the universe **decreases** when one mole of liquid water converts to one mole of water vapor at 25°C.

We can repeat this calculation in terms of the free energy change:

$$\Delta(G) = \Delta(H) - T\Delta(S)$$

$$\Delta(G) = 44000 \frac{\text{J}}{\text{mol}} - (298.15 \text{ K}) \left(118.9 \frac{\text{J}}{\text{K mol}} \right)$$

$$\Delta(G) = 8.55 \frac{\text{kJ}}{\text{mol}} > 0$$

Since the free energy increases in the transformation of one mole of liquid water to one mole of water vapor, we predict that the transformation will not occur spontaneously. This is something of a relief, because we have correctly predicted that the mole of liquid water is stable at 25°C relative to the mole of water vapor.

We are still faced with our perplexing question, however. Why does any water evaporate at 25°C? How can this be a spontaneous process?

The answer is that we have to be careful about interpreting our prediction. The entropy of one mole of water vapor at 25°C **and 1.00 atm pressure** is $188.8 \frac{\text{J}}{\text{K}}$. We should clarify our prediction to say that one mole of liquid water will not spontaneously evaporate to form one mole of water vapor at 25°C and 1.00 atm pressure. This prediction is in agreement with our observation, because we have found that the water vapor formed spontaneously above liquid water at 25°C has pressure 23.8 torr, well below 1.00 atm.

Assuming that our reasoning is correct, then the spontaneous evaporation of water at 25°C when **no** water vapor is present initially must have $\Delta(G) < 0$. And, indeed, as water vapor forms and the pressure of the water vapor increases, evaporation must continue as long as $\Delta(G) < 0$. Eventually, evaporation stops in a closed system when we reach the vapor pressure, so we must reach a point where $\Delta(G)$ is no longer less than zero, that is, evaporation stops when $\Delta(G) = 0$. This is the point where we have equilibrium between liquid and vapor.

We can actually determine the conditions under which this is true. Since $\Delta(G) = \Delta(H) - T\Delta(S)$, then when $\Delta(G) = 0$, $\Delta(H) = T\Delta(S)$. We already know that $\Delta(H) = 44.0 \text{ kJ}$ for the evaporation of one mole of water. Therefore, the pressure

of water vapor at which $\Delta(G) = 0$ at 25°C is the pressure at which $\Delta(S) = \frac{\Delta(H)}{T} = 147.6 \frac{J}{K}$ for a single mole of water evaporating. This is larger than the value of $\Delta(S)$ for one mole and 1.00 atm pressure of water vapor, which as we calculated was $118.9 \frac{J}{K}$. Evidently, $\Delta(S)$ for evaporation changes as the pressure of the water vapor changes. We therefore need to understand why the entropy of the water vapor depends on the pressure of the water vapor.

Recall that 1 mole of water vapor occupies a much smaller volume at 1.00 atm of pressure than it does at the considerably lower vapor pressure of 23.8 torr. In the larger volume at lower pressure, the water molecules have a much larger space to move in, and therefore the number of microstates for the water molecules must be larger in a larger volume. Therefore, the entropy of one mole of water vapor is larger in a larger volume at lower pressure. The entropy change for evaporation of one mole of water is thus greater when the evaporation occurs to a lower pressure. With a greater entropy change to offset the entropy loss of the surroundings, it is possible for the evaporation to be spontaneous at lower pressure. And this is exactly what we observe.

To find out how much the entropy of a gas changes as we decrease the pressure, we assume that the number of microstates W for the gas molecule is proportional to the volume V . This would make sense, because the larger the volume, the more places there are for the molecules to be. Since the entropy is given by $S = k \ln(W)$, then S must also be proportional to $\ln(V)$. Therefore, we can say that

Equation:

$$\begin{aligned} S(V_2) - S(V_1) &= R \ln(V_2) - R \ln(V_1) \\ &= R \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

We are interested in the variation of S with pressure, and we remember from Boyle's law that, for a fixed temperature, volume is inversely related to pressure. Thus, we find that

Equation:

$$\begin{aligned} S(P_2) - S(P_1) &= R \ln\left(\frac{P_1}{P_2}\right) \\ &= - \left(R \ln\left(\frac{P_2}{P_1}\right) \right) \end{aligned}$$

For water vapor, we know that the entropy at 1.00 atm pressure is $188.8 \frac{J}{K}$ for one mole. We can use this and the equation above to determine the entropy at any other pressure. For a pressure of 23.8 torr = 0.0313 atm, this equation gives that

$S(23.8 \text{ torr})$ is $217.6 \frac{J}{K}$ for one mole of water vapor. Therefore, at this pressure, the $\Delta(S)$ for evaporation of one mole of water vapor is $217.6 \frac{J}{K} - 69.9 \frac{J}{K} = 147.6 \frac{J}{K}$. We can use this to calculate that for evaporation of one mole of water at 25°C and water vapor pressure of 23.8 torr is $\Delta(G) = \Delta(H) - T\Delta(S) = 44.0 \text{ kJ} - (298.15 \text{ K}) (147.6 \frac{J}{K}) = 0.00 \text{ kJ}$. This is the condition we expected for equilibrium.

We can conclude that the evaporation of water when no vapor is present initially is a spontaneous process with $\Delta(G) < 0$, and the evaporation continues until the water vapor has reached its the equilibrium vapor pressure, at which point $\Delta(G) = 0$.

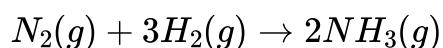
Thermodynamic description of reaction equilibrium

Having developed a thermodynamic understanding of phase equilibrium, it proves to be even more useful to examine the thermodynamic description of reaction equilibrium to understand why the reactants and products come to equilibrium at the specific values that are observed.

Recall that $\Delta(G) = \Delta(H) - T\Delta(S) < 0$ for a spontaneous process, and $\Delta(G) = \Delta(H) - T\Delta(S) = 0$ at equilibrium. From these relations, we would predict that most (but not all) exothermic processes with $\Delta(H) < 0$ are spontaneous, because all such processes increase the entropy of the surroundings when they occur. Similarly, we would predict that most (but not all) processes with $\Delta(S) > 0$ are spontaneous.

We try applying these conclusions to synthesis of ammonia

Equation:



at 298K, for which we find that $\Delta(S^\circ) = -198 \frac{J}{\text{mol K}}$. Note that $\Delta(S^\circ) < 0$ because the reaction reduces the total number of gas molecules during ammonia synthesis, thus reducing W , the number of ways of arranging the atoms in these molecules.

$\Delta(S^\circ) < 0$ suggests that [\[link\]](#) should not occur at all. However, $\Delta(H^\circ) = -92.2 \frac{\text{kJ}}{\text{mol}}$. Overall, we find that $\Delta(G^\circ) = -33.0 \frac{\text{kJ}}{\text{mol}}$ at 298K, which according to [\[link\]](#) suggests that [\[link\]](#) is spontaneous.

Given this analysis, we are now pressed to ask, if [\[link\]](#) is predicted to be spontaneous, why does the reaction come to equilibrium without fully consuming all of the reactants? The answer lies in a more careful examination of the values given: $\Delta(S^\circ)$, $\Delta(H^\circ)$, and $\Delta(G^\circ)$ are the values for this reaction **at standard conditions**, which

means that all of the gases in the reactants and products are taken to be at 1 atm pressure. Thus, the fact that $\Delta(G^\circ) < 0$ for [\[link\]](#) at standard conditions means that, if all three gases are present at 1 atm pressure, the reaction will spontaneously produce an increase in the amount of NH_3 . Note that this will reduce the pressure of the N_2 and H_2 and increase the pressure of the NH_3 . This changes the value of $\Delta(S)$ and thus of $\Delta(G)$, because as we already know the entropies of all three gases depend on their pressures. As the pressure of NH_3 increases, its entropy decreases, and as the pressures of the reactant gases decrease, their entropies increase. The result is that $\Delta(S)$ becomes increasingly negative. The reaction creates more NH_3 until the value of $\Delta(S)$ is sufficiently negative that $\Delta(G) = \Delta(H) - T\Delta(S) = 0$.

From this analysis, we can say by looking at $\Delta(S^\circ)$, $\Delta(H^\circ)$, and $\Delta(G^\circ)$ that, since $\Delta(G^\circ) < 0$ for [\[link\]](#), reaction equilibrium results in production of more product and less reactant than at standard conditions. Moreover, the more negative $\Delta(G^\circ)$ is, the more strongly favored are the products over the reactants at equilibrium. By contrast, the more positive $\Delta(G^\circ)$ is, the more strongly favored are the reactants over the products at equilibrium.

Thermodynamic Description of the Equilibrium Constant

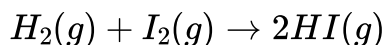
Thermodynamics can also provide a quantitative understanding of the equilibrium constant. Recall that the condition for equilibrium is that $\Delta(G) = 0$. As noted before, $\Delta(G)$ depends on the pressures of the gases in the reaction mixture, because $\Delta(S)$ depends on these pressures. Though we will not prove it here, it can be shown by application of [\[link\]](#) to a reaction that the relationship between $\Delta(G)$ and the pressures of the gases is given by the following equation:

Equation:

$$\Delta(G) = \Delta(G^\circ) + RT \ln(Q)$$

(Recall again that the superscript $^\circ$ refers to standard pressure of 1 atm. $\Delta(G^\circ)$ is the difference between the free energies of the products and reactants when all gases are at 1 atm pressure.) In this equation, Q is a quotient of partial pressures of the gases in the reaction mixture. In this quotient, each product gas appears in the numerator with an exponent equal to its stoichiometric coefficient, and each reactant gas appears in the denominator also with its corresponding exponent. For example, for the reaction

Equation:



Equation:

$$Q = \frac{P_{HI}^2}{P_{H_2}P_{I_2}}$$

It is important to note that the partial pressures in Q need not be the equilibrium partial pressures. However, if the pressures in Q are the equilibrium partial pressures, then Q has the same value as K_p , the equilibrium constant, by definition. Moreover, if the pressures are at equilibrium, we know that $\Delta(G) = 0$. If we look back at [\[link\]](#), we can conclude that

Equation:

$$\Delta(G^\circ) = -(RT \ln(K_p))$$

This is an exceptionally important relationship, because it relates two very different observations. To understand this significance, consider first the case where $\Delta(G^\circ) < 0$. We have previously reasoned that, in this case, the reaction equilibrium will favor the products. From [\[link\]](#) we can note that, if $\Delta(G^\circ) < 0$, it must be that $K_p > 1$. Furthermore, if $\Delta(G^\circ)$ is a large negative number, K_p is a very large number. By contrast, if $\Delta(G^\circ)$ is a large positive number, K_p will be a very small (though positive) number much less than 1. In this case, the reactants will be strongly favored at equilibrium.

Note that the thermodynamic description of equilibrium and the dynamic description of equilibrium are complementary. Both predict the same equilibrium. In general, the thermodynamic arguments give us an understanding of the conditions under which equilibrium occurs, and the dynamic arguments help us understand how the equilibrium conditions are achieved.

Review and Discussion Questions

Exercise:**Problem:**

Each possible sequence of the 52 cards in a deck is equally probable. However, when you shuffle a deck and then examine the sequence, the deck is never ordered. Explain why in terms of microstates, macrostates, and entropy.

Exercise:

Problem:

Assess the validity of the statement, "In all spontaneous processes, the system moves toward a state of lowest energy." Correct any errors you identify.

Exercise:**Problem:**

In each case, determine whether spontaneity is expected at low temperature, high temperature, any temperature, or no temperature:

$$\Delta(H^\circ) > 0, \Delta(S^\circ) > 0$$

$$\Delta(H^\circ) < 0, \Delta(S^\circ) > 0$$

$$\Delta(H^\circ) > 0, \Delta(S^\circ) < 0$$

$$\Delta(H^\circ) < 0, \Delta(S^\circ) < 0$$

Exercise:**Problem:**

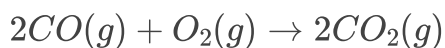
Using thermodynamic equilibrium arguments, explain why a substance with weaker intermolecular forces has a greater vapor pressure than one with stronger intermolecular forces.

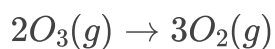
Exercise:**Problem:**

Why does the entropy of a gas increase as the volume of the gas increases? Why does the entropy decrease as the pressure increases?

Exercise:**Problem:**

For each of the following reactions, calculate the values of $\Delta(S^\circ)$, $\Delta(H^\circ)$, and $\Delta(G^\circ)$ at $T = 298K$ and use these to predict whether equilibrium will favor products or reactants at $T = 298K$. Also calculate K_p .

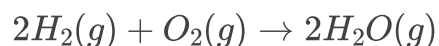




Exercise:

Problem:

Predict the sign of the entropy for the reaction



Give an explanation, based on entropy and the Second Law, of why this reaction occurs spontaneously.

Exercise:

Problem:

For the reaction $H_2(g) \rightarrow 2H(g)$, predict the sign of both $\Delta(H^\circ)$ and $\Delta(S^\circ)$. Should this reaction be spontaneous at high temperature or at low temperature? Explain.

Exercise:

Problem:

For each of the reactions in [\[link\]](#), predict whether increases in temperature will shift the reaction equilibrium more towards products or more towards reactants.

Exercise:

Problem:

Using [\[link\]](#) and [\[link\]](#), show that for a given set of initial partial pressures where Q is larger than K_p , the reaction will spontaneously create more reactants. Also show that if Q is smaller than K_p , the reaction will spontaneously create more products.